

EMISSION OF SULPHUR DIOXIDE BY THERMOOXIDATION OF ESTONIAN OIL SHALE AND COAL

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Abstract. This article describes the dynamics of sulphur dioxide emission during the thermooxidation of Estonian oil shale and coal and their mixtures with the mass ratio 1 : 1 as well as the influence of oil shale ash addition on the dynamics. Thermogravimetric equipment developed for absorption of the emitted gases and titration of the solution was used. It was established that the share of emitted SO_2 decreases from 35–75% by the thermooxidation of coal and its mixtures with oil shale to 7–35% for samples with oil shale ash addition.

Key words: oil shale, coal, sulphur dioxide, air pollution.

1. INTRODUCTION

Due to high sulphur content ($\sim 1.5\%$), the production of power and shale oil from Estonian oil shale (EOS) causes environmental pollution with sulphur compounds. About 20–40% of the total sulphur, contained in oil shale, is emitted during combustion of oil shale at thermal power plants [1]. In the production of shale oil, approximately 50% of the total sulphur is volatilized, the remainder is accumulated in the solid residue (semicoke), partially in the form of sulphide [2,3]. As a result of oxidation and hydration during semicoke storage in the dumps, sulphides turn into watersoluble sulphur compounds, known as dangerous contaminants of soil, waterbodies and groundwater [4].

The transformation of sulphur compounds at high-temperature combustion of oil shale (at the flame temperature 1200–1400 °C) has been described by Ots et al. [5]. The results of investigations of thermal destruction of different oil shales in neutral and oxidational gaseous areas were reported in [6–13]. In fact, these investigations do not deal with the dynamics of SO_2 emission during thermo-

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

This paper presents the results of the investigations of SO₂ emission during thermooxidation of EOS, of different samples of coal and their mixtures as well as the influence of oil shale ash addition on the dynamics of SO₂ evolution.

2. EXPERIMENTAL

One sample of EOS and five different samples of coal were investigated. Different forms of sulphur (total, pyritic and sulphate) in the fuels were determined according to [14]. The content of organic sulphur was calculated as:

$$S_{\text{org}} = S_{\text{total}} - S_{\text{pyr}} - S_{\text{sulph}}$$

and the content of organic matter in dry samples as:

$$[100 - A^d - (\text{CO}_2)_M^d], \%$$

where A^d is oil shale ash addition.

The content of sulphur in the sample of oil shale calculated on dry basis was 1.63%, of which 74% was pyritic sulphur, 6% sulphate, and 20% organic sulphur. Coal samples differ in the content of total sulphur as well as in the forms of the latter. Furthermore, the content of their mineral part differs (Table). The content of sulphur varies in the range of 0.43–7.04%, of which the content of pyritic sulphur forms from 0 (coal 3) to 46% (coal 5), sulphate from 7.3 (coal 4) to 37% (coal 2) and the content of organic sulphur from 41.6 (coal 2) to 93% (coal 4) of the total sulphur.

Characteristics of fuels (dry basis)

Sample	Organic matter, %	Content, %						
		(CO ₂) _M	CaCO ₃	FeS ₂	S _{pyr}	S _{sulph}	S _{org}	S _{total}
Coal 1	90.0	0.94	2.1	<0.10	<0.025	<0.10	0.305	0.43
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
Coal 5	91.7	1.27	2.9	0.86	0.46	0.13	0.42	1.01
Oil shale	32.0	19.75	44.9	2.24	1.20	<0.10	0.33	1.63

In the sample of EOS, the content of organic matter was 32.0% and in those of coal, between 87.2–91.7%. For the sample of EOS, the gross heat of combustion was 10.26, for those of coal, between 25.54–30.77 MJ per kg.

Our experiments were carried out by the help of thermogravimetric equipment (Q-Derivatograph, MOM) under dynamic heating conditions (5 K per min) in a stream of air up to 900°C with absorption of the evolved gases and titration of the solution at pH 4.0 [15,16]. That enabled a simultaneous fixation of the thermogravimetric (TG) curve, the derivative TG (DTG) curve, the differential thermal analysis (DTA) curve, the thermal gas titrimetry (TGT), and the derivative TGT (DTGT) curve. Multiplate Pt-crucibles were used, the mass of the samples was 275–325 mg. In the solid residue, the content of the total sulphur was determined. In the mixtures of fuels with oil shale ash, the mole ratio of free CaO/SO₂ varied from 1.0 to 4.3 (the SO₂ content was calculated, based on the total sulphur content in the fuels) and was regulated by the amount of oil shale ash added. The low-temperature oil shale ash, formed at 600–900°C during the experimental combustion of EOS in the bubbling fluidized bed boiler (Ahtme), was used. The content of total CaO in the ash was 66.2%, free CaO – 45.2%, carbonate CaO – 1.5%, MgO – 6.9%, total sulphur – 2.3%, and SiO₂ – 7.7%.

3. RESULTS AND DISCUSSION

The differences in the behaviour of EOS, in the samples of coal and their mixtures during thermooxidation were observed. Thermooxidation of EOS started at 250°C and continued up to 540°C with two intensive exoeffects, accompanied by mass losses with a maximum on the DTA curve at 340 and 460°C (Fig. 1). The first exoeffect corresponds to the thermooxidation of the lighter part of volatile matter, the second one to the thermooxidation of the heavier part of organic matter [7,8] and pyrite [17]. The endoeffect with a minimum on the DTA curve at 780°C corresponds to the decomposition of carbonates in the mineral part of oil shale, which started at 580–600°C and lasted up to 820–850°C. The total mass loss up to 540°C was 30.5%, which well corresponds to the content of organic matter and organic and pyritic sulphur in oil shale (Table). Up to 850°C, the mass loss was 51.7%. The results differ from those obtained by Kundel et al. [8] (exoeffects with a maximum on the DTA curve at 325 and 467°C, mass loss at 540°C – 36.3%) because of the differences in the content and composition of the organic and mineral parts of the samples used.

The emission of SO₂ in EOS started at 300°C, with a maximum on the DTGT curve at 340 and 480°C and with shoulders at 420 and 540°C. At 600°C, 51.5% of the total content of sulphur was evolved. SO₂ emission at the temperature interval from 300 to 400°C originates from the destruction of the lighter part of organic matter, at 400–600°C – from the destruction of the heavier part of the organic matter and pyrite. The maximum on the DTGT curve at 480°C for EOS well corresponds to the maximum on the DTGT curve for pyrite studied in similar experimental conditions.

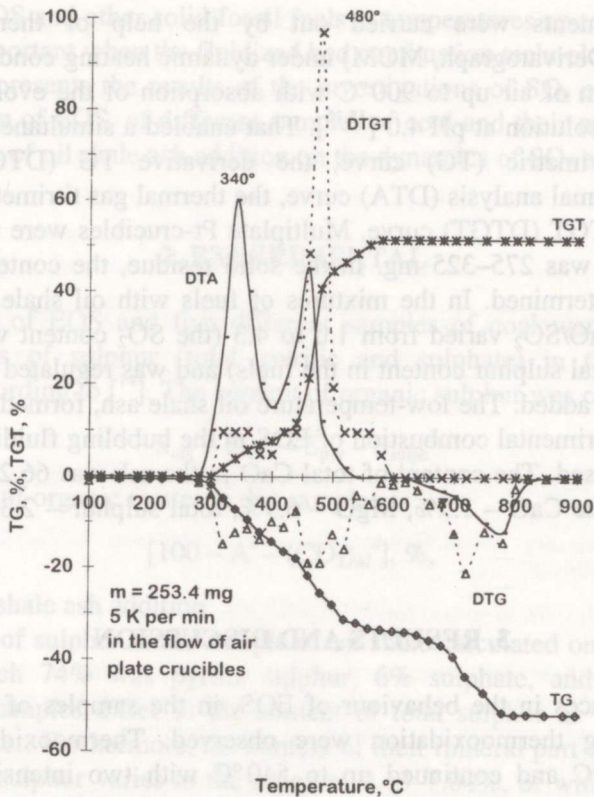


Fig. 1. Thermogram of Estonian oil shale.

The thermooxidation of the samples of coal and their mixtures with EOS started at 200–300°C and continued up to 600–650°C, with two or three exoeffects, accompanied by mass losses. For example, the decomposition of coal 4 took place in the temperature range from 280 to 620°C. Three exoeffects, with the accompanying mass losses at 360, 480 and 560°C, were fixed. Up to 620°C, the mass loss was 90.9% of the total mass of the sample. The emission of SO₂ started at 320°C and lasted up to 620°C, with maximas on the DTGT curve at 450 and 540°C. Up to 72.6% of the total content of sulphur was evolved (Fig. 2a). At the thermogram of coal 4 and oil shale mixture, two exoeffects were observed, accompanied by mass losses with maximas at 300 and 480–500°C. The latter had two shoulders, at 410 and 450°C. The mass loss up to 600°C was 72.2% from the total mass of the sample. The emission of SO₂ took place at the temperature interval of 300–600°C, with maximas on the DTGT curve at 340, 420 and 500°C. In sum, 49.3% of the total content of sulphur was evolved (Fig. 2b).

To model the recirculation of ash in the circulating fluidized bed (CFB), in part of our experiments, the ash formed by burning EOS at the Ahtme bubbling (periodical) fluidized bed combustor (which corresponds to the newly formed

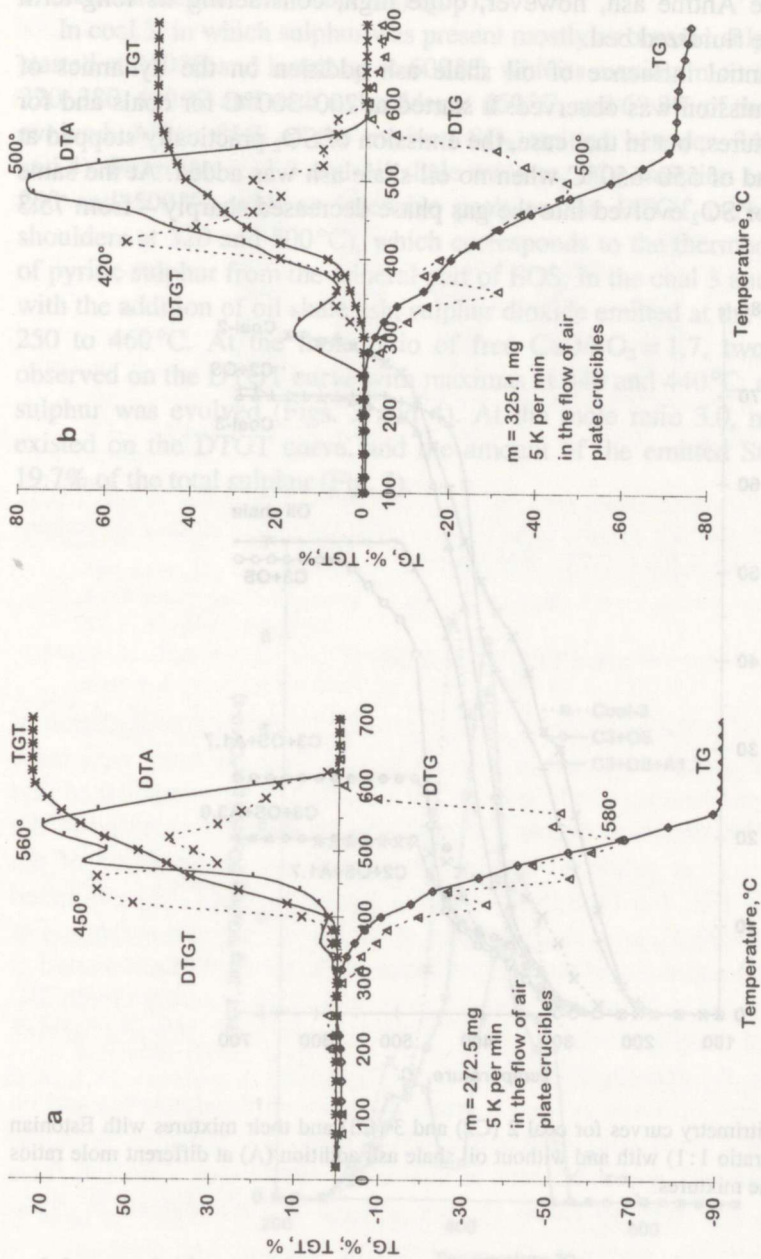


Fig. 2. Thermograms of coal 4 (a) and the coal 4 and Estonian oil shale mixture (mass ratio 1:1) (b).

ash in CFB) was used. The Ahtme ash was characterized by a high SO_2 binding capacity – 72 mg SO_2 per 100 mg sample. In our experiments, this ash was compared with the oil shale ash formed by the combustion of EOS in CFB at the H. Ahlström Laboratory [18]. The SO_2 binding capacity of the latter sample was half of that of the Ahtme ash, however, quite high, considering its long-term recirculation in the fluidized bed.

Thus, a substantial influence of oil shale ash addition on the dynamics of sulphur dioxide emission was observed. It started at 200–300 °C for coals and for coal–oil shale mixtures, but in that case, the emission of SO_2 practically stopped at 480–500 °C, instead of 550–650 °C when no oil shale ash was added. At the same time, the amount of SO_2 evolved into the gas phase decreased sharply – from 75.3 to 7.1% (Fig. 3).

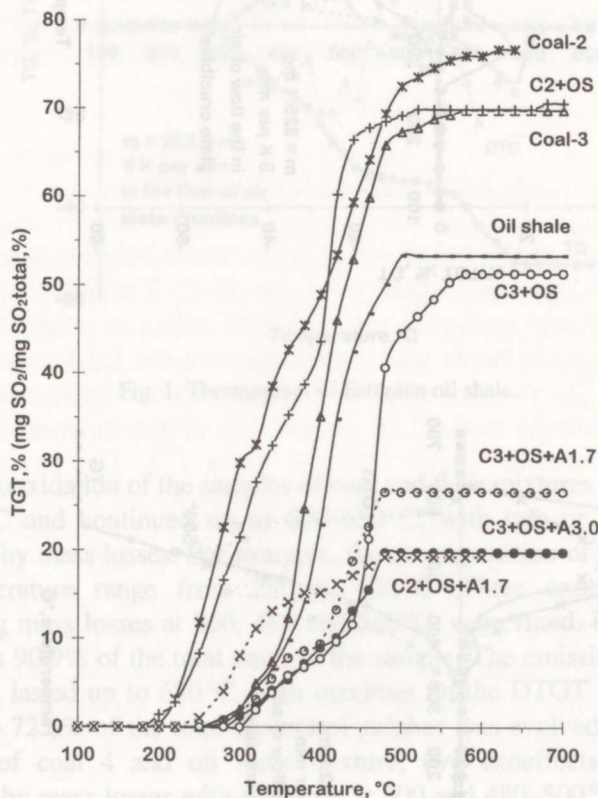


Fig. 3. Thermal gas titrimetry curves for coal 2 (C2) and 3 (C3) and their mixtures with Estonian oil shale (OS) (mass ratio 1:1) with and without oil shale ash addition (A) at different mole ratios of free CaO/SO_2 in the mixtures.

For example, during thermooxidation of coal 2 (with the highest sulphur content), SO_2 emission started at 200 °C and lasted in four steps up to 600 °C, 75.3% of the total sulphur was evolved. In the mixture of coal 2 and EOS, SO_2

emission also began at 200°C, but stopped at 520°C, and the amount of the evolved SO₂ corresponded to 70.6% of the total sulphur. In the coal 2 and oil shale mixture, with the addition of oil shale ash in the amount required to reach the mole ratio free CaO/SO₂ = 1.7, SO₂ emission was completed at 460°C, whereas 19.3% of the total sulphur was evolved (Fig. 3).

In coal 3, in which sulphur was present mostly as organic sulphur, SO₂ emission started at 250°C and lasted up to 600°C, with its maximum on the DTGT curve at 320, 380, 420°C and with a shoulder at 460°C, and 69.8% of the total sulphur was evolved. About 85% of the evolved SO₂ emitted between 340–520°C (Figs. 3 and 4). From the coal 3 and oil shale mixture, SO₂ emission took place between 260 and 500°C, with an intensive peak on the DTGT curve at 420°C (with shoulders at 320 and 500°C), which corresponds to the thermooxidative emission of pyritic sulphur from the mineral part of EOS. In the coal 3 and oil shale mixture with the addition of oil shale ash, sulphur dioxide emitted at the temperatures from 250 to 460°C. At the mole ratio of free CaO/SO₂ = 1.7, two low peaks were observed on the DTGT curve with maximas at 340 and 440°C, and 26.5% of total sulphur was evolved (Figs. 3 and 4). At the mole ratio 3.0, no intensive peaks existed on the DTGT curve, and the amount of the emitted SO₂ was limited to 19.7% of the total sulphur (Fig. 3).

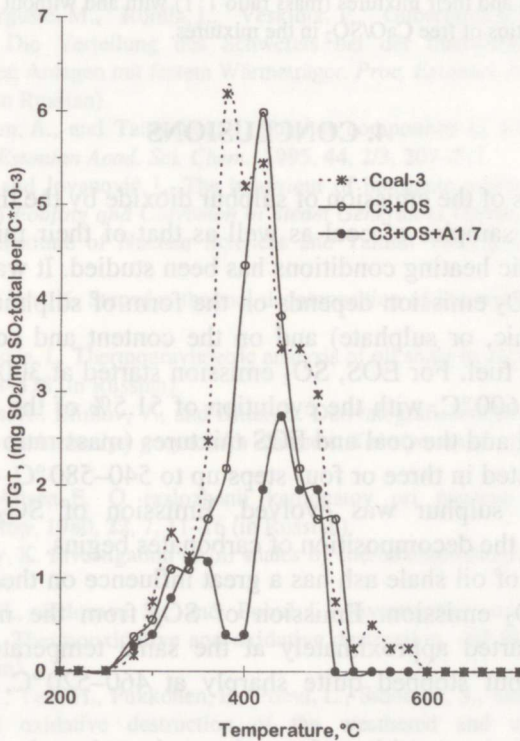


Fig. 4. Derivative thermal gas titrimetry curves of the coal 3 (C3) and Estonian oil shale (OS) mixtures (mass ratio 1:1) with and without oil shale ash addition (A) at the mole ratio of free CaO/SO₂ = 1.7.

The influence of oil shale and oil shale ash addition on the distribution of sulphur between the solid and gas phases by thermooxidation of coal is demonstrated in Fig. 5. Emission of SO_2 diminishes from 63.7% for coal 1 to 54.2% for the coal 1 and oil shale mixture, and to 11.1 and 7.3% for the coal 1 and oil shale mixture with oil shale ash addition at the mole ratios of free $\text{CaO}/\text{SO}_2 = 1.7$ and 4.3, respectively.

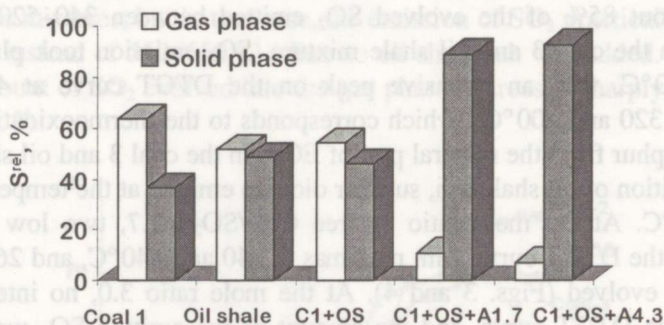


Fig. 5. Distribution of sulphur between solid and gas phases during combustion of coal 1 (C1), Estonian oil shale (OS) and their mixtures (mass ratio 1:1) with and without oil shale ash addition (A) at different mole ratios of free CaO/SO_2 in the mixtures.

4. CONCLUSIONS

1. The dynamics of the emission of sulphur dioxide by the thermooxidation of EOS and different samples of coal as well as that of their mixtures with mass ratio 1:1 in dynamic heating conditions has been studied. It was established that the dynamics of SO_2 emission depends on the form of sulphur contained in the fuel (pyritic, organic, or sulphate) and on the content and composition of the mineral part of the fuel. For EOS, SO_2 emission started at 300°C and continued in two steps up to 600°C , with the evolution of 51.5% of the total sulphur. For the samples of coal and the coal and EOS mixtures (mass ratio 1:1), it started at $200\text{--}320^\circ\text{C}$ and lasted in three or four steps up to $540\text{--}580^\circ\text{C}$, during which 35–75% of the total sulphur was evolved. Emission of SO_2 stopped at the temperatures when the decomposition of carbonates begins.

2. The addition of oil shale ash has a great influence on the dynamics and on the amount of SO_2 emission. Emission of SO_2 from the mixtures with the addition of ash started approximately at the same temperatures as for fuels without addition, but stopped quite sharply at $460\text{--}520^\circ\text{C}$, instead of $550\text{--}650^\circ\text{C}$.

Depending on the composition of a coal sample and on the mole ratio of free CaO/SO_2 in the fuel and ash mixtures (from 1.0 to 4.3), the amount of the

evolved SO₂ decreased from 35–75% without the addition of ash to 7–35% with ash addition.

At the mole ratio of free CaO/SO₂ = 1.7 in the mixture, 80–90% of the total sulphur content was bound in the solid (ash). The increase in the mole ratio from 1.7 to 4.3 was followed by an additional 5–10% increase in the amount of the bound sulphur in the solid phase.

3. The results of these investigations give evidence of the possibility and efficiency of a significant reduction of sulphur dioxide emission into the atmosphere as a result of the combustion of sulphur-rich coal in the mixture with EOS, in particular, when using the CFB technique. This can provide a prerequisite for enriching the Estonian power industry with new sources of fuels.

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VÄÄVELDIOKSIIDI EMISSION EESTI PÕLEVKIVI JA KIVISÜTE TERMOOKSÜDATSIOONIL

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Kasutades termogravimeetria meetodit koos eralduvate gaaside absorbeerimise ning tiitrimisega, uuriti vääveldioksiidi emissiooni dünaamikat Eesti põlevkivi, erinevate kivisüte ja nende segude termooksüdatsioonil ning põlevkivituha lisandite mõju sellele. Tehti kindlaks, et SO₂ emissioon gaasifaasi tahkekütuste termooksüdatsioonil väheneb olenevalt kasutatud kivisööst, selle segust põlevkiviga ning vaba CaO/SO₂ moolsuhtest segus (vahemikus 1,0–4,3) 35–75%-lt tuhalisandita proovides kuni 7–35%-ni tuhalisandiga proovides.