



Experimental analysis of the combustion characteristics of Estonian oil shale in air and oxy-fuel atmospheres



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ABSTRACT

A non-isothermal experimental study using thermogravimetric analysis and differential scanning calorimetry coupled with a quadrupole mass spectrometer was conducted to investigate Estonian oil shale combustion characteristics. The analyses were performed in air (N₂/O₂) and oxy-fuel (CO₂/O₂) atmospheres with various oxygen ratios (10, 20 and 30 vol.%). Our experimental results in TGA show that combustion in the CO₂/O₂ atmosphere is delayed compared to that in the N₂/O₂ atmosphere. Carbonate minerals in oil shale decompose in air in one step and in the oxy-fuel atmosphere in two separate steps: the decomposition of dolomite (CaMg(CO₃)₂) and the subsequent decomposition of calcite (CaCO₃). An increased oxygen ratio in combustion in the oxy-fuel atmosphere increases the overall combustion rate, whereas the CO₂ emission volumes decrease because of the lower decomposition extent of carbonates. The quadrupole mass spectrometer measurements indicate several combustion products. A higher CO reading is registered in the CO₂/O₂ atmosphere, but there is no other significant difference. Based on the measurement results, a combustion model for Estonian oil shale is proposed. Combustion in the oxy-fuel atmosphere is similar to combustion in air, which eases the design of oxy-fuel combustors.

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1. Introduction

The world's growing demand for energy enforces the usage of low-grade fuels. In Estonia, oil shale (OS) power and oil production sectors are the largest CO₂ emitters. Estonia depends on OS because over 90% of its electricity is produced from OS [1,2]. Therefore, improving the OS combustion process has large environmental and economic benefits.

OS is a low-grade fossil fuel that consists of kerogen (organic) and mineral components. The organic matter contains a relatively large amount of hydrogen, and the H/C atomic ratio is 1:4–1:5 [3]. Estonian OS has a high content of mineral matter, which consists of carbonaceous, sandy-clay-carbonaceous and sandy-clay parts [4]. A higher CO₂ concentration can alter the decomposition of carbonates and decrease CO₂ emission [5]. Therefore, implementation of oxy-fuel technology offers many benefits.

The most energy- and cost-effective CCS technology is considered to be the oxy-fuel technology [6]. Implementing the carbon capture and storage (CCS) systems on oxy-fuel combustion technology significantly reduces CO₂ emission. The concept of the oxy-fuel technology is the removal of nitrogen from the combustion process, that is, combustion occurs in an oxygen and carbon dioxide atmosphere. As a result, the

formed flue gas mainly consists of carbon dioxide and water vapor, and the volume of flue gas considerably decreases [7,8].

Previous studies [5,9–14] concluded that a higher carbon dioxide concentration in the combustion atmosphere decreases the decomposition of carbonate minerals in the OS, but to our best knowledge, there is no data about higher CO₂ atmosphere effects on the combustion of OS kerogen. Thermogravimetric analysis (TGA) of coal oxy-fuel combustion has proven that the oxy-fuel atmosphere considerably changes the combustion process [15–18]. Nevertheless, Niu and co-workers considered that the investigation of the reaction mechanism and kinetic parameters of the oxy-fuel combustion of coal are not sufficiently reviewed [15]. The same applies to OS oxy-fuel combustion.

Simultaneous use of TGA, DSC and QMS allow one to obtain more data with higher precision from different processes that occur in the OS during the thermal treatment. TGA is a common technique to rapidly investigate and compare thermal events and kinetics during the combustion and pyrolysis of a material [19]. TGA measures the mass loss of the sample as a function of time and temperature. A quadrupole mass spectrometer (QMS) improves the analyses of the processes by adding information about the evolving gases. The temperatures at which the mass changes occur can be viewed using TGA, and quantitative methods can be applied to the data to obtain the kinetic parameters. DSC adds thermal information about the processes that occur during the measurement, and QMS detects the evaporating ions.

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This paper provides detailed information about all of the steps of OS combustion in air and oxy-fuel atmospheres and compares the obtained results with the existing model.

2. Experiment

2.1. Materials

All experiments were conducted with an OS sample that was obtained from an underground mine in Estonia and was provided by the Eesti Power Plant. The OS sample was dried and crushed to pass through a sieve with 1 mm openings. The mineral composition of the OS sample is shown in Table 1, and the chemical composition and laboratory ash analysis are shown in Table 2.

2.2. Equipment and procedures

The thermal analyses were performed on a Netzsch STA 449 F3 Jupiter Simultaneous Thermal Analyzer (TG–DSC/DTA Apparatus), which was coupled with a Netzsch QMS 403D Aeolos (mass 1–300 amu). The samples were analyzed in Pt/Rh crucibles with a lid and a removable liner composed of thin-walled Al_2O_3 in the gas flows, as shown in Fig. 1. In the combustion experiments, approximately 20 mg of the oil shale sample was used. The total gas flow during all measurements was 60 ml/min. In the TGA, the oil shale samples were heated to 1240 °C, with a heating rate of 10 K/min. The instrument temperature and heat sensitivity were calibrated with In, Sn, Zn, Al and Au standards. The produced gases were analyzed using QMS during the entire heating process. The mass/charge (m/z) values of 8–150 were collected with a sampling rate of 0.2 s/ m/z . All measurements were performed at least twice for sufficient reproducibility. The used material was non-homogeneous. Nevertheless, notably good reproducibility was achieved.

2.3. Visual inspection of the product oil shale ash

No visual differences among different ash samples from various experiments were noticed after removing the samples from the TG/DSC apparatus. As expected, all of the samples were slightly sintered at this high temperature (1240 °C) but remained easily removable with a small brush.

2.4. Characteristic parameters of the combustion and decomposition of carbonates

The following characteristic parameters that were previously used by researchers [15,16,20] were measured using the TGA: ignition temperature T_i ; temperatures of the maximum mass loss rate $T_{\text{max}1}$ and $T_{\text{max}2}$; burn-out temperature T_b . These parameters describe the thermal behavior of the OS's organic part.

The following parameters for the carbonate decomposition were obtained: beginning temperature T_{d1} of the reaction; temperature of the maximum mass loss rate $T_{\text{max}3}$; and ending temperature T_{e1} of the carbonate decomposition. In the CO_2/O_2 atmosphere, the decomposition of carbonate minerals occurs in two steps. The beginning temperature T_{d2} of the second decomposition step, temperature of the maximum mass loss rate $T_{\text{max}4}$ and ending temperature T_{e2} of the second step were measured. The identical parameters were obtained using DSC, and some differences were noticed.

Table 1
Mineral composition of the Estonian oil shale sample, wt%.

Dolomite	Calcite	Quartz	K-feldspar	Illite	Chlorite	Kaolinite	Pyrite	Sum
18.6	41.8	12.1	5.87	16.4	1.77	tr.	3.27	99.9

Table 2
Elemental composition of the OS and the laboratory ash.

Oil shale	%	Oil shale ash	%
$\text{CO}_2^{\text{d carb}}$	20.12	SiO_2^{d}	30.74
H^{d}	2.90	FeO_3^{d}	4.84
C^{d}	27.90	$\text{Al}_2\text{O}_3^{\text{d}}$	6.08
N^{d}	0.02	CaO^{d}	39.00
S^{d_0}	1.20	MgO^{d}	8.68
$\text{S}^{\text{d}_{\text{sulphate}}}$	0.08	$\text{K}_2\text{O}^{\text{d}}$	1.81
$\text{S}^{\text{d}_{\text{sulphide}}}$	1.12	$\text{Na}_2\text{O}^{\text{d}}$	0.13
		Ash $_{815^\circ\text{C}}$	47.0
Q_b^{d}	10.038 MJ/kg		

2.5. Oil shale combustion model

It has been suggested that a six-step mechanism can describe the OS combustion mechanism [21,22]. Potentially, the following reaction steps occur:

1. water removal,
2. decomposition of kerogen,
3. dissociation of volatile matter into bitumen and gases,
4. oxidation of volatile matter,
5. oxidation of fixed carbon, and
6. decomposition of carbonate minerals.

The scope of the reaction steps depends on the specific OS, but all of the reaction steps should be noticeable during the measurement. TG–DSC–QMS analysis is used to further investigate the reaction steps.

3. Results and discussion

The plots of the TG, DTG and DSC measurements in different N_2/O_2 and CO_2/O_2 mixtures (Fig. 1) are shown in Fig. 2.

The measurements are shown in Table 3 and Fig. 3 and will be analyzed.

3.1. Overall combustion analysis

According to the earlier presented theory [21,22], the first combustion step is the separation of water vapor. Many researchers [21, 23–26] suggest that even with an air-dry material, a small mass loss is observed in the temperature range of 60 to 200 °C, which is connected to the evaporation of water. In addition to moisture, the OS contains crystal water (clay minerals, such as illite, chlorite, and kaolinite,

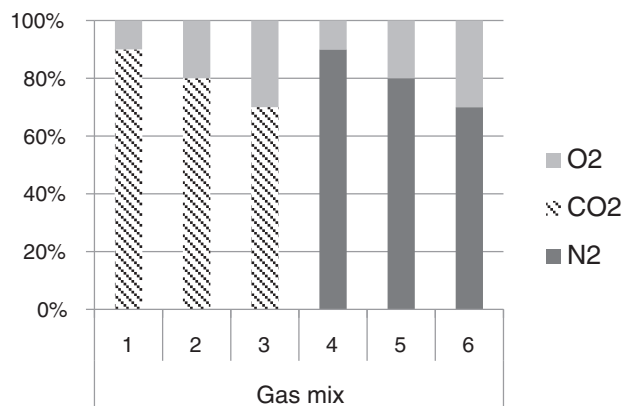


Fig. 1. Gas mixtures in the experiments.

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