

EVOLVED GAS ANALYSIS AT THERMAL TREATMENT OF OIL SHALES BY TG-FTIR

T. KALJUVEE, E. and EDRO, R. KUUSIK
Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn Estonia,
e-mail tiidu@staff.ttu.ee

ABSTRACT

TA technique combined with FTIR equipment was used for comparative estimation of the thermal behavior of samples with simultaneous identification of gaseous compounds formed and emitted at thermooxidation of oil shale samples from different deposits (Estonia, Israel, Jordan, Morocco). The experiments were carried out under dynamic heating conditions up to 900°C at heating rates of 5, 10 or 50 K min⁻¹ in a stream of dry air. In addition to CO₂ and H₂O as major gases evolved a number of individual volatile species like CO, SO₂, COS, methane, ethane, ethylene, formaldehyde, acetaldehyde, formic acid, methanol, chlorobenzene, etc. were determined. Notable differences in the composition of gaseous compounds evolved as well as differences in the absorbance of individual species in FTIR spectra depending on the origin of fuel and on the heating rate used were determined.

INTRODUCTION

The combustion of solid fossil fuels in industrial boilers leads to the contamination of atmosphere with different toxic and environmentally unfriendly compounds as CO₂, CO, SO₂, Volatile Organic Compounds (VOCs), and Polycyclic Aromatic Hydrocarbons (PHAs).

60% of the total energy production in Estonia and 95% of the electricity production, which is concentrated into the Estonian and Baltic Power Plants, is based on combustion of Estonian oil shale (EOS). Up to 2004 these power plants operated on the high-temperature (1200-1400°C) combustion of pulverized EOS only, but since 2004 the two energy blocks with circulating fluidized bed combustion (CFBC) boilers (780-820°C) have been implemented which is more suitable technology for low grade fuels. The data published in [Lahtvee, 2000] confirmed that the contamination of atmosphere in Estonia with VOCs, including PHAs [Ots, 1992], formed at Narva power plants at high-temperature combustion of EOS is not very high - on the level of 200 - 300 tons per year. It indicated that VOCs formed during incomplete firing of EOS were decomposed and oxidized almost completely before leaving the boiler. But when using FBC technique for combustion of solid fossil fuels the firing temperature is much lower and the conditions for formation and preservation of VOCs at that are more suitable.

The use of TG-DTA technique combined with FTIR is an efficient tool for identification of gaseous compounds evolved at thermal treatment of fuels in neutral [Carangelo, 1987; Zanier, 1999; Strezov, 2004] as well as in oxygen [Pitkänen, 1999; Lu, 1999; Kaljuvee, 2004] atmosphere. The goal of current research was the precise and comparative thermal characterization of low grade oil shale samples from different deposit (Estonia, Jordan, Israel, Morocco) with identification of gaseous compounds formed and emitted by using TG-FTIR technique.

MATERIALS AND METHODS

Materials

Two samples of EOS and one sample of Jordanian (JOS), Israeli (IOS) and Moroccan (MOS) oil shale were studied.

Using different methods of chemical analyses, the chemical composition as well as the gross calorific (high heating) value (calorimeter B-08BM) of these samples was determined and is presented in Table 1. For element analyses (Vario EL analyzer) the previously air-dried and ground samples were supplementary dried at 105°C for 24 hours.

The content of organic matter and fixed carbon in the dry samples was calculated as:

$$[100 - A^d - (CO_2)_M^d], \%$$

where A^d is the content of ash, %; $(CO_2)_M^d$ is the content of mineral carbon dioxide, %, both on dry bases.

Oil shale samples studied are characterized by low content of organic matter - between 17-30% - except EOSII (63%) being almost pure kerogen and, respectively, with high content of mineral matter - 70-83% (EOSII - 37%). The content of mineral CO_2 indicated the high content of carbonates - calcite, dolomite - in oil shale samples (Table 1). The content of sulfur varied from 1.22% (EOSII) to 3.52% (JOS), including at that pyritic, organic and sulphate sulfur; the content of hydrogen varied from 1.46% (IOS) to 5.96% (EOSII) (Table 1).

There were no significant differences observed in the mole ratio of $(H/C)^{total}$ for oil shale samples studied (between 1.02 and 1.27, for EOSII - 1.47) (Table 1), but the much higher mole ratio of H/C^{org} calculated - between 1.50 and 1.62 - indicated at that the probability for formation of VOCs at thermal treatment of samples.

Table 1. Main characteristics of sample (on dry bases)

Content, wt.%	EOS I	EOS II	JOS	IOS	MOS
Organic matter	29.7	63.1	22.6	17.1	18.5
Ash	50.5	32.1	61.9	60.3	66.4
$(CO_2)_M$	19.8	5.8	15.5	22.6	15.1
S_{total}	1.63	1.22	3.52	2.60	1.97
S_{pyr}	1.20	0.47	0.28	0.88	0.34
S_{sulph}	0.10	0.04	0.12	0.32	0.10
S_{org}	0.33	0.71	3.12	1.40	1.53
N	0.53	0.09	0.42	0.39	0.50
H	3.00	5.96	2.24	1.46	1.65
C	28.3	48.5	22.2	17.1	16.3
$(H/C)^{mole}_{total}$	1.27	1.47	1.21	1.02	1.21
Gross Calorific Value, MJ kg ⁻¹	10.24	22.43	8.14	4.90	---

METHODS

The TG-FTIR system consisted of Setaram *Labsys* 2000 equipment coupled to the Interspec 2020 Fourier Transform Infrared Spectrometer by a transfer line. The Ranger-AIP Gas Cell, S/N 23790, (REFLEX Analytical Co) with 8.8 m path length and KBr windows were used. Both, the transfer line and the gas cell were heated to 150°C to prevent condensation. The gas cell was equipped with DTSG (deuterated triglycine sulphate) detector cooled with liquid nitrogen. FTIR measurements were recorded in the 4000-600 cm^{-1} region with a resolution of 4 cm^{-1} and 4 scans as an average. The Bio-Rad (Sadtler) Know. It All search program and Gases & Vapors Database (code GS) and Organics& Polymers Database (code TU, SR) were used.

The experiments were carried out under dynamic heating conditions up to 900°C at heating rates of 5, 10 or 50 K per minute in a stream of dry air (70 mL min^{-1}). In case of using the heating rate of 50°C min^{-1} , the final temperature was held constant during 15 minutes. Setaram *Labsys* 2000 enabled simultaneous fixation of TG, DTG and DTA data. Standard 100 μL Pt-crucibles were used; the mass of samples depending on the content of organic matter in the samples used was 20-30 mg.

RESULTS AND DISCUSSION

Thermal analyses

The thermooxidation of oil shale samples proceeded in three steps. Firstly, thermooxidation of volatile organic compounds, secondly, thermooxidation of heavier part of organic matter (kerogen) as well as thermooxidation of pyrite and, finally, decomposition of carbonates [Pitkänen, 1999; Kaljuvee, 2004; Kök, 2001; Cebulak, 1999; Paulik, 1982; Jorgensen, 1982].

At the heating rates of 5 and 10°C min^{-1} the emission of adsorbed water and gaseous species proceeded up to 150-180°C and the mass loss at that was for oil shale samples studied in the range of 0.9-2.5% (Figure 1). At the heating rate of 50°C min^{-1} it continued up to 200-230°C with the mass loss of 1-8.5% (Figure 2). The first step of thermooxidation of organic matter lasted, depending on the origin of the sample, up to 375-450°C (Figure 1, 3, 4), indicating the differences in the composition of organic matter of oil shale samples, and being the lowest for JOS and the highest for EOSII. The second step of thermooxidation of organic matter lasted up to 520-565°C and for EOS II, being rich in kerogen, even up to 685°C (Figure 4). However, the boundary between the first and second step of thermooxidation of organic matter could not be always clearly defined and it depends very much on the origin of the sample and the heating rate used being quite similar to the result presented in [Kök, 2001, Cebulak, 1999]. The total mass loss considering both steps of thermooxidation was for samples studied 20.5-63.5% being definitely the highest for EOS II.

The third step of thermooxidation of the OS samples is mainly related to the decomposition of carbonates which can be followed by the endoeffect with the minimum at 720-808°C in DTA curves (Figure 3 and 4). The mass loss was completed at 740-820°C and the total mass loss at that varied between 41.7% (JOS) and 68.5% (EOS II).

The peaks in DTA curves of EOS II at 302°C, 352°C, 483°C (Figure 3) and at 348°C, 409°C, 588°C (Figure 4) heated up at the heating rate of 5°C and 10°C/ min^{-1} , respectively, demonstrate well the complexity of decomposition of organic matter (kerogen). The extremely complicated chemical composition of kerogen in EOS is well proved in [Lille, 2002].

At the heating rate of 50°C min^{-1} the first and the second step of thermooxidation was better differentiated for the samples in which organic matter contains more volatile compounds – Estonian OS, Jordanian OS (Table 1). For example, the maxima of exoeffects in DTA curves at 346°, 522°, and 630° for EOSII are clearly separated by a deep minimum between them at 497° and 535°C (Figure 5). The peak maxima at 522°C in DTA curve of EOSII corresponds to thermooxidation of pyrite. The peak maxima in DTA and DTG curves as well as the boundary between the first and the second step of thermooxidation were shifted 50-90°C towards higher temperatures compared to lower heating rate

(Figure 1-5) being at that in a good correlation with the results published in [Strezov, 2004; Lu, 1999; K ok, 1998]. But it was not possible clearly to differentiate the second and the third step in OS samples resulting from the incomplete thermooxidation of the heavier part of kerogen before beginning of the decomposition of carbonates at the higher heating rate. The mass loss was completed after up to twelve (EOSII) minutes of holding the samples at 900 C (Figure 2 and 5). The total mass loss for samples was at that 4-5% smaller than at low heating rates (Figure 1 and 2) which could have been caused by the incomplete changes within the mineral part of samples or/and partial binding of gaseous species (SO₂, CO₂, HCl) formed and evolved during thermooxidation of the samples, for an example, by free Ca, Mg-oxides formed during the decomposition of carbonates or by silicates [Kaljuvee, 1999; Kaljuvee, Kuusik, 2004; Xie, 1999; Liu, 2000].

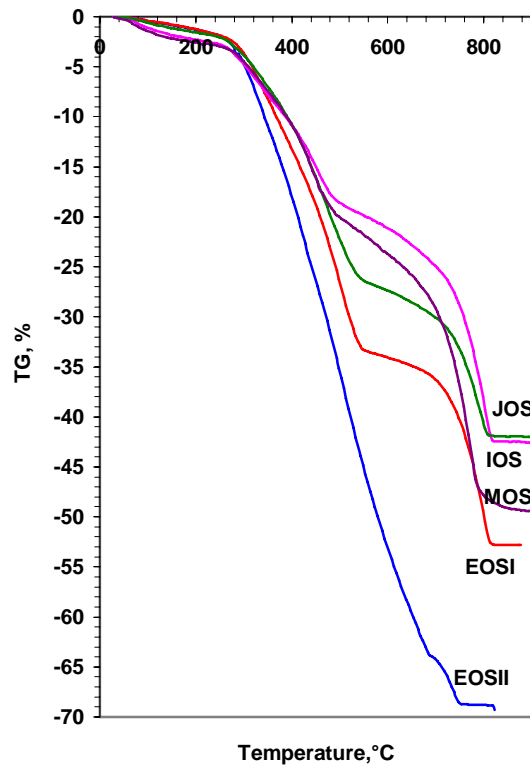


Fig. 1 TG curves of oil shale samples thermooxidated at a heating rate of 10  C min⁻¹

FTIR analyses

The list of gaseous compounds evolved at the thermooxidation of oil shale samples studied differed lightly from each other depending on the origin of fuel. More differences were observed in the intensities of characteristic peaks of different species evolved in FTIR spectra depending on the origin of fuel as well as on the heating rate of thermooxidation which were in a good correlation with the results described earlier in [Pitkänen, 1999; Lu, 1999; Kaljuvee, 2004].

A part of FTIR spectra of gaseous compounds evolved at different temperatures during the TG scan of fuel samples studied at heating rate of $10^{\circ}\text{C min}^{-1}$ is presented in Figures 6-8. The two major gaseous compounds evolved at thermooxidation of oil shale samples were CO_2 and H_2O . The appearance of the characteristic water bands in FTIR spectra in broad ranges $3900\text{-}3500\text{ cm}^{-1}$ and $1900\text{-}1300\text{ cm}^{-1}$ and the characteristic peaks for CO_2 (2380 and 678 cm^{-1}) below $180\text{-}200^{\circ}\text{C}$ indicated the emission of water and carbon dioxide adsorbed in the samples. The presence of water absorption bands in these ranges causes the overlapping of characteristic peaks of the other gas species at higher temperatures complicating at that the identification of them.

In addition to CO_2 and water the characteristic peaks for CO (2178 and 2113 cm^{-1}), acetic (1798 and 1176 cm^{-1}) and formic (1749 and 1108 cm^{-1}) acids, formaldehyde (1749 and 1706 cm^{-1}) and acetaldehyde (1763 and 1420 cm^{-1}), ketons (1719 cm^{-1}), SO_2 (1375 and 1362 cm^{-1}), ethane (2970 and 1458 cm^{-1}) and chlorobenzene (1473 cm^{-1} and 742 cm^{-1}) were clearly fixed in FTIR spectra of all the samples studied (Figure 6-8).

The characteristic peaks for methane (3016 and 1307 cm^{-1}), HCl (absorption bands in broad ranges $3000\text{-}2700\text{ cm}^{-1}$), COS (2074 and 2052 cm^{-1}), methanol (1034 and 1008 cm^{-1}), ethanol (1244 and 1052 cm^{-1}), ethylene (1648 cm^{-1} and 950 cm^{-1}), *p*-xylene (1512 and 793 cm^{-1}), NH_3 (967 and 933 cm^{-1}), and possibly furan (746 cm^{-1}) were identified also in FTIR spectra of most of samples (Figure 6-8). The emission of HCl at thermooxidation of fuel samples was proved by appearing of characteristic absorption bands at $240\text{-}330^{\circ}\text{C}$ at $3000\text{-}2700\text{ cm}^{-1}$ which at higher temperatures could be overlapped (or disappeared) with more intensive bands of other compounds evolved.

Comparing the FTIR spectra of different samples it can be observed that these of IOS and MOS (Figure 8) were a little bit poorer and the characteristic peaks for many organic compounds in the FTIR spectra were usually less intensive than these for EOS and JOS samples (Figure 6 and 7). At that the characteristic peaks for ethylene, methanol, and ethanol in the FTIR spectra of IOS and MOS were presented on the level of traces, the characteristic peaks for NH_3 in FTIR spectra of MOS (Figure 8) were absent at all. These differences in the intensities of characteristic peaks of different compounds evolved at thermooxidation of oil shale samples in FTIR spectra could be explain by the differences in the content of organic matter, especially by the differences in element composition of samples (Table 1).

The influence of the heating rate

The beginning of emission of most gaseous compounds formed at thermooxidation of the samples studied at heating rates of 5 and $10^{\circ}\text{C min}^{-1}$ was fixed in the interval of $180\text{-}250^{\circ}\text{C}$, but some of them like *p*-xylene and chlorobenzene at $250\text{-}300^{\circ}\text{C}$ (Figure 6-8).

At $5^{\circ}\text{C min}^{-1}$ heating rate the temperature of maximum intensities of characteristic peaks of COS, ethane and methane was $300\text{-}350^{\circ}\text{C}$ (Figure 9), of ethylene, ethanol, formaldehyde, and formic acid $350\text{-}400^{\circ}\text{C}$ (Figure 10), of CO, acetic acid and acetaldehyde $400\text{-}450^{\circ}\text{C}$ and of SO_2 , *p*-xylene, and chlorobenzene $450\text{-}500^{\circ}\text{C}$ (Figure 11-12).

At $10^{\circ}\text{C min}^{-1}$ the temperature of maximum intensities of characteristic peaks of COS and ethane was 350°C , of CO, ethanol, formaldehyde, methane and formic acid $400\text{-}450^{\circ}\text{C}$, of ethylene, acetaldehyde and acetic acid 450°C and of SO_2 , *p*-xylene and chlorobenzene $500\text{-}550^{\circ}\text{C}$ the

temperatures being shifted by 50-150°C towards higher temperatures as compared to these at the heating rate of 5°C min⁻¹ (Figure 9-12).

During thermooxidation of Jordanian oil shale samples at 5 and 10°C min⁻¹ heating rates the emission of methanol occurred in one step with maximum intensity in FTIR spectra at 350°C and 400°, respectively, and of the other oil shale samples in two steps with maximums at 300-350°C and 450-500°C, respectively .

At the heating rate of 50°C min⁻¹ the emission of the most of gaseous compounds formed started at 250-300°C and of p-xylene and chlorobenzene at 350-400°C being shifted by 50-70°C towards higher temperatures as compared to lower heating rates. The most of gaseous compounds evolved at that in two steps. The temperatures of maximum intensities of characteristic peaks of COS, CO, methane, ethane, methanol, and ethanol were 400-500°C and 650-800°C, of formic and acetic acid, form- and acetaldehyde 600-700°C, of two ethylene peaks 450-500°C and 700-800°C, of SO₂, p-xylene and chlorobenzene 450-600°C and 800-900°C (Figure 9-12). So, the temperatures of maximum intensities of characteristic peaks were shifted by 70-300°C and 150-450°C towards higher temperatures as compared to heating rates of 10 and 5°C min⁻¹, respectively, and for most of the species evolved the intensities of respective absorption bands increased together with the increase in the heating rate (Fig. 9-12). It could be caused by the circumstance that at higher heating rates the contact-time between organic gaseous compounds formed at thermooxidation of solid fossil fuels and oxygen shortens and is not enough for the complete oxidation of these species before they leave the furnace.

CONCLUSIONS

The use of TA technique coupled with FTIR measurement enabled not only to determine the differences in the thermal behavior of oil shale samples, but also to identify a number of individual volatile species formed and emitted at thermooxidation of samples. The differences in the composition of gaseous compounds evolved and in the intensities of the absorption bands of these species in FTIR spectra depending on the origin of fuels and on the heating rate were established.

At 5°C min⁻¹ heating rate the temperature of maximum intensities of characteristic peaks of COS, ethane, and methane was 300-350°C, of ethylene, ethanol, NH₃, formaldehyde, and formic acid 350-400°C, of CO, acetic acid and acetaldehyde 400-450°C and of SO₂, p-xylene and chlorobenzene 450-500° being at that, as a rule, more intensive for EOS and JOS samples. Thus, a good correlation between the absorbance of bands characteristic to VOCs evolved and the elemental composition of the samples was observed.

At 10 and 50°C min⁻¹ the temperatures of maximum intensities of characteristic peaks of different gaseous species evolved were shifted by 50-150°C and 150-450°C, respectively, towards higher temperatures as compared to these at the heating rate of 5°C min⁻¹, and for most of the species evolved the intensities of respective absorption bands increased together with the increase in the heating rate.

Acknowledgement

This work was partly supported by the Estonian Science Foundation (G5606).

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