CHEMICAL ENGINEERING TRANSACTIONS

VOL. 81, 2020

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš
Copyright © 2020, AIDIC Servizi S.r.l.
ISBN 978-88-95608-79-2; **ISSN** 2283-9216

DOI: 10.3303/CET2081143

Surface Characterisation of Estonian Oil Shale Semi-Coke

Heliis Pikkor*, Heidi Lees, Birgit Maaten, Oliver Järvik, Alar Konist

Tallinn University of Technology, Department of Energy Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
heliis.pikkor@taltech.ee

Oil shale is a low-grade fossil fuel that has been used in Estonia mostly for electricity and shale oil production. The conventional use of oil shale results in a vast amount of carbon dioxide emissions urging to find alternative ways for sustainable utilisation of oil shale and develop new technologies. Since oil shale contains relatively high amount of organic matter it should be suitable for producing porous carbonised material (semi-coke) that has high surface area and can be used as an adsorbent in various applications. The aim of this research is to determine the effect of thermal treatment conditions on the specific surface area (SSA) of semi-coke. Estonian oil shale from Ojamaa underground mine was pyrolysed in a batch reactor using different temperatures in the range of 550 to 900 °C and atmospheres (N_2 and CO_2). The surface properties (BET SSA, pore volume and pore size distribution) of obtained samples were studied using N_2 adsorption. The results showed that when the pyrolysis temperature was raised in N_2 environment, larger SSA of the sample was obtained – it increased from 12 m^2/g (pyrolysed at 550 °C) to 31 m^2/g (pyrolysed at 900 °C). At higher temperatures the increase of pores less than 5 nm in diameter was also noticed. The semi-coke samples prepared in N_2 environment had larger SSA compared to the ones prepared in CO2.

1. Introduction

Oil shale has been one of the most important natural resources in Estonia for over a century. It has been mostly used for electricity and shale oil production (Konist et al., 2018). Nowadays the industry is heading more towards oil production as oil shale represents a large and mostly unused hydrocarbon resource (Maaten et al., 2020).

Oil shale has relatively high content of organic matter called kerogen (Neshumayev et al., 2019). After thermal treatment kerogen decomposes and firstly forms bitumen that further decomposes into oil, gas and semi-coke residue (Rajeshwar, 1981). Semi-coke has been mostly considered as a waste product of shale oil production. Depending on the technology, it is either landfilled (Pihu et al., 2019) or combusted within the process (Han et al., 2014). However, depending on the pyrolysis conditions this carbonised material can have quite high surface area and could be suitable to use as a raw material to prepare adsorbents for purification of aqueous solutions (Nassef and Eltaweel, 2019) or flue gases (Dupre et al., 2018).

The effect of thermal treatment conditions on oil shale semi-coke porosity has been studied previously. (Bai et al., 2012) studied the effects of final pyrolysis temperature on Huadian oil shale in the low-temperature range up to 550 °C. Higher temperature and slower heating rate promoted the development of pores as the surface area increased from 5 to 48 m^2/g. (Han et al., 2011) used oil shale from Dachengzi mine to study the effect of temperature, heating rate, residence time etc in the temperature range from 430 to 520 °C. They found that raising the temperature up to 490 °C caused pore opening which resulted in higher surface areas.

Besides temperature, pyrolysis atmosphere can also affect the porosity. Although nitrogen is mostly used as the environment, (Guo et al., 2020) have successfully used pure oxygen for pyrolysis atmosphere at low temperatures. Using carbon dioxide has proven to improve surface area and porosity development in some cases (Valdés et al., 2018). (Luo et al., 2019) noted that pyrolysing coal in CO_2 atmosphere had a positive effect on increasing the pore volume and surface area. Surface area increased from 123.6 to 152.4 m^2/g when N_2 was substituted with CO_2. (Borrego et al., 2009) noted the same effect when using wood chips as a raw material. (Gao et al., 2013) compared coal chars prepared in pure N_2 and in mixed environment of 50 % N_2 and 50 % CO_2. Adding CO_2 to the mixture promoted coal pyrolysis, causing decrease in char yield and increase in the amount of volatiles that led to chars with higher surface areas.

Paper Received: 30/04/2020; Revised: 24/05/2020; Accepted: 31/05/2020
Please cite this article as: Pikkor H., Lees H., Maaten B., Järvik O., Konist A., 2020, Surface Characterisation of Estonian Oil Shale Semi-Coke, Chemical Engineering Transactions, 81, 853-858 DOI:10.3303/CET2081143

The aim of this paper is to characterise Estonian oil shale semi-coke produced at different temperatures and in different gaseous environments and study the effect of pyrolysis conditions on semi-coke pore formation and surface properties. This research is aimed to create a fundamental base to continue studying the suitability of Estonian oil shale semi-coke as a raw material to produce adsorbents.

2. Experimental

2.1 Materials

Oil shale used for the pyrolysis experiments was obtained from Ojamaa underground mine located in northeast Estonia. Elemental composition of untreated oil shale is shown in Table 1 as received dry basis. Before thermal treatment, oil shale was crushed and sieved to obtain sample with particle size in the range of 250-500 µm.

Table 1: Elemental composition and organic carbon content of oil shale.

	C, wt%	H, wt%	N, wt%	S, wt%	TOC, wt%
Oil shale	25.8	2.5	0.1	1.7	20.6

TOC – calculated based on total carbon content and inorganic carbon content

2.2 Semi-coke preparation

Semi-coke samples were prepared by pyrolysing oil shale under different conditions in an electrically heated batch reactor (Figure 1). Firstly, the reactor was heated to the desired temperature and was allowed to stabilise for 20 minutes. Approximately 5 g of oil shale was inserted into the balance chamber and flushed with carrier gas (N_2 or CO_2) for 5 minutes to eliminate residual air. After that, the sample was dropped into the reactor at preset temperature and kept in there for 20 minutes under a gas flow of 0.3 L/min. The sample was then taken out of the reactor and left to cool in the balance chamber that was again flushed with carrier gas.

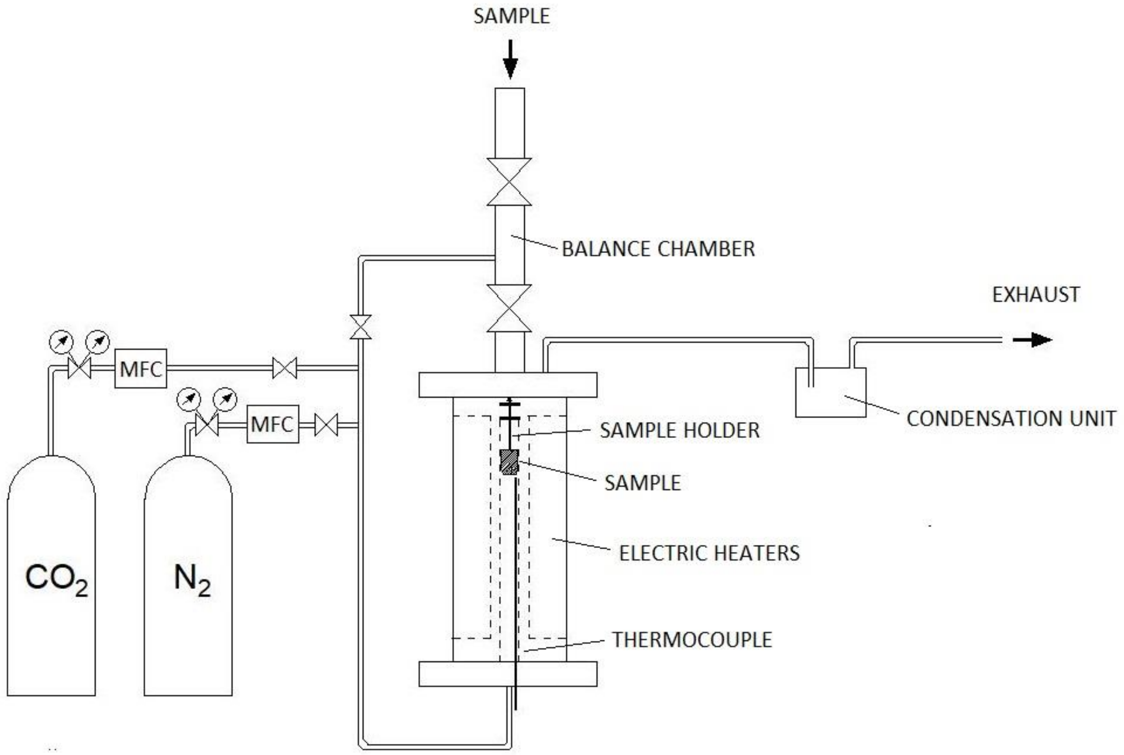


Figure 1: Simplified scheme of the pyrolysis reactor

The effect of pyrolysis temperature on the SSA of semi-coke was studied in N_2 atmosphere using three different temperatures – 550 °C, 750 °C and 900 °C (samples named SC550, SC750 and SC900). The effect of pyrolysis atmosphere on porous structure was studied at 750 °C while varying the gaseous environment – besides using N_2, a mixture of 50 % N_2 and 50 % CO_2 and pure CO_2 was used (samples named SC750 N_2/CO_2 and SC750

CO_2 accordingly). Three experiments were conducted in each condition, remaining solid semi-coke was mixed together to obtain average sample for further analysis.

2.3 Measurements

The surface area, pore volume and pore size distribution of obtained semi-coke samples were investigated by using the N_2 adsorption-desorption method at -196 °C with Quantachrome Autosorb iQ apparatus. N_2 adsorption was measured in the relative pressure (P/P_0) range of 0.0001 to 0.99. The semi-coke samples (approximately 0.5 g) were degassed at 300 °C for 24 hours to remove surface impurities. The specific surface area (SSA) was calculated by applying the BET (Brunauer-Emmett-Teller) method on data points from the linear part of the adsorption isotherm (usually in the P/P_0 range of 0.05 to 0.3). Pore size distribution was determined using Density Functional Theory (DFT). The International Union of Pure and Applied Chemistry (IUPAC) suggests that pores with diameters over 50 nm should be called macropores, pores with diameters in the range of 2-50 nm should be called mesopores and pores with diameters under 2 nm should be called micropores (Sing, 1985). Total pore volume was determined by the amount of N_2 adsorbed at relative pressure $P/P_0=0.99$. Micropore volume was calculated using Dubinin-Radushkevich (DR) model in the relative pressure P/P_0 range of 0.0001 to 0.1.

Scanning electron microscope (SEM) images were taken with Zeiss EVO/MA15 apparatus to further study the surface morphology of prepared semi-cokes.

Elementar Vario MACRO Cube elemental analyser with SoliTIC module was used to measure the elemental composition and total inorganic carbon (TIC) content to evaluate the total organic carbon (TOC) content.

3. Results and discussion

3.1 Isotherm analysis

According to IUPAC, most of physisorption isotherms can be divided into six characteristic types. The isotherm shapes of samples SC550, SC750 and SC900 are shown on Figure 2. All analysed oil shale semi-cokes produced similar N_2 adsorption-desorption isotherms. The shape is similar to Type II isotherms, which indicates that oil shale semi-cokes have mostly meso- and macroporous structure. While SC550 and SC750 produce almost identical shape, SC900 adsorption capacity increases steeply at relative pressure $P/P_0 > 0.9$. This rise can be attributed to the increase of macroporosity. In general, the adsorption capacity of semi-cokes increased when treated at higher temperatures.

The presence of hysteresis can also be seen from the adsorption-desorption isotherms. Hysteresis is usually associated with capillary condensation in mesoporous structures. The shape of hysteresis loop is believed to be related to the porous structure of the sample, indicating the pore shape. Hysteresis loops of given samples are similar to type H3, which means the pore shape is most likely slit.

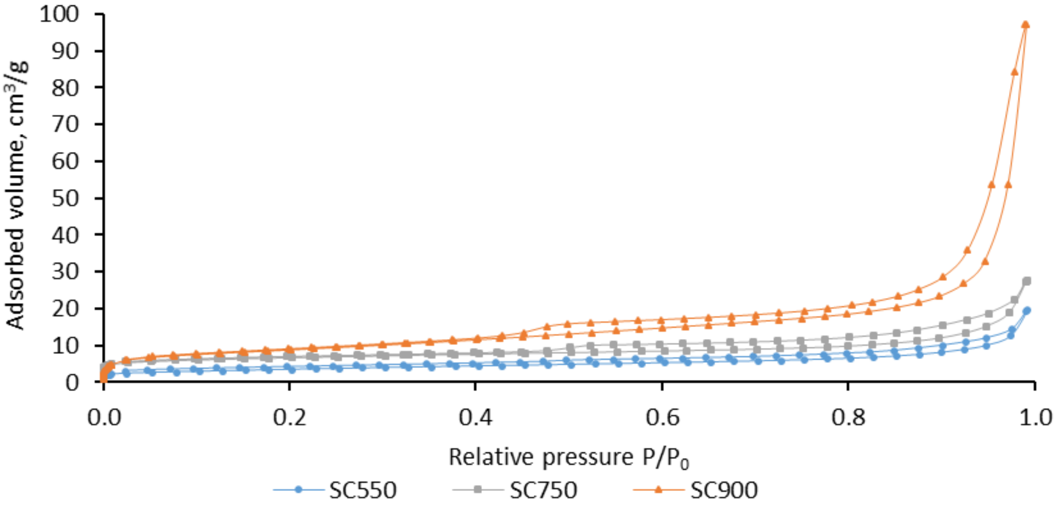


Figure 2: Adsorption-desorption isotherms of semi-cokes prepared at 550, 750 and 900 °C in N2 atmosphere

3.2 Effect of pyrolysis temperature

Total pore volume, micropore volume and BET surface area of produced semi-cokes are shown in Table 2. Raising temperature from 550 to 750 °C increased the SSA almost twice – from 12.5 to 24.0 m^2/g. The change in total pore volume was rather small, but the micropore volume increased more than two times. This indicates that higher microporosity is the reason behind the surface area increase. Raising temperature from 750 to 900 °C resulted also in SSA increase from 24 to 31 m^2/g. Total pore volume increased more than three times, but micropore volume did not change significantly. It shows that at 900 °C the development of micropores was slightly inhibited and mostly larger pores formed when oil shale was exposed to higher temperature.

During thermal treatment of oil shale particles, the porous structure undergoes changes due to volatile release. As temperature of oil shale particles increases, kerogen starts to decompose and pressure inside the particles rises. High pressure gases suddenly erupt from the inside causing the opening of pore mouths and promoting the development of porous surface (Han et al., 2006). Thermal treatment at 550 °C seemed to remove kerogen only partially as more organic carbon remained in the sample (Table 2). This might be the reason for smaller surface area as some pores did not open properly in these conditions. At 900 °C faster and more extensive volatile release occurred, resulting in larger surface area.

Table 2: Total carbon and total organic carbon content, total pore volume, micropore volume and BET surface area of semi-cokes prepared at different temperatures

Sample	Gaseous atmosphere	C, wt%	TOC, wt%	Total pore volume, cm^3/g	Micropore volume, cm^3/g	BET surface area, m^2/g
SC550	100 % N_2	12.2	5.3	0.030	0.004	12.5
SC750	100 % N_2	9.7	4.1	0.043	0.009	24.0
SC900	100 % N_2	6.3	3.0	0.150	0.010	31.3

The effect of pyrolysis temperature on semi-coke pore size distribution can be seen in Figure 3. The pore size distribution of SC550 and SC750 is fairly similar although growth in number of pores smaller than 5 nm can be noticed. Further increase in temperature to 900 °C clearly promotes the development of pores smaller than 5 nm even more. Most significant is the rise of the amount of ~1 nm micropores in SC900. The amount of larger pores (i.e. mesopores larger than 15 nm) grew substantially in sample SC900.

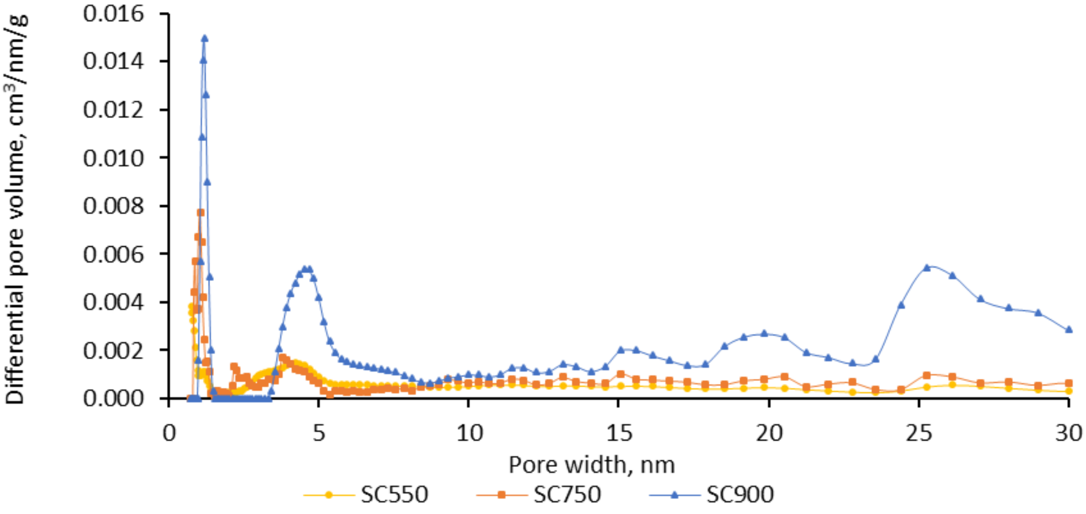
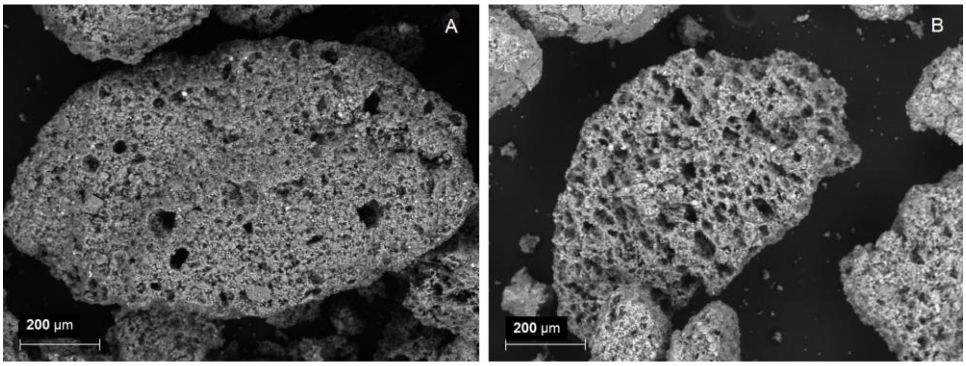


Figure 3: Differential pore volume distribution of oil shale semi-cokes prepared at different temperatures in N_2

SEM micrographs of semi-cokes prepared at 550 °C and 900 °C are presented in Figure 4. These images give visual evidence that thermal treatment at higher temperatures results in the opening of pore mouths and promotes the development of more complex porous networks. At 550 °C many pores have remained closed, resulting in smaller surface area. At 900 °C presence of a clearly more developed porous structure can be seen.



(a) (b)

Figure 4: SEM images (magnification 250x) of semi-cokes prepared in N_2 at (a) 550 °C (b) and 900 °C

3.3 Effect of pyrolysis atmosphere

The effect of atmosphere on semi-coke surface properties can be seen in Table 3. The results showed that when changing the pyrolysis environment from N_2 to CO_2 the BET area of semi-coke decreased almost twice – from 24 to 13 m^2/g. As (Loo et al., 2015) have noted, processes in CO_2 environment tend to take longer. The formation of porous network is more time consuming in CO_2 as the release of organic matter takes longer and some pore mouths remain closed after thermal treatment. The results in Table 3 also confirmed that semi-cokes prepared in mixed environment and pure CO_2 contained more organic carbon compared to the one prepared in N_2.

Table 3: Total carbon and total organic carbon content, total pore volume, micropore volume and BET surface area of semi-cokes prepared in different atmospheres.

Sample	Gaseous atmosphere	C, wt%	TOC, wt%	Total pore volume, cm^3/g	Micropore volume, cm^3/g	BET surface area, m^2/g
SC750	100 % N_2	9.7	4.1	0.043	0.009	24.0
SC750 N_2/CO_2	50/50 % N_2/CO_2	10.7	5.1	0.035	0.006	15.3
SC750 CO_2	100 % CO_2	10.7	5.4	0.036	0.005	13.0

The pore size distribution of samples is fairly similar for mesopores larger than 5 nm (Figure 5). Main difference can be seen in the amount of smaller mesopores and micropores. Adding CO_2 to pyrolysis environment caused a decrease of pores smaller than 5 nm. Micropore volume of sample SC750 CO_2 decreased almost two times compared to semi-coke prepared in N_2.

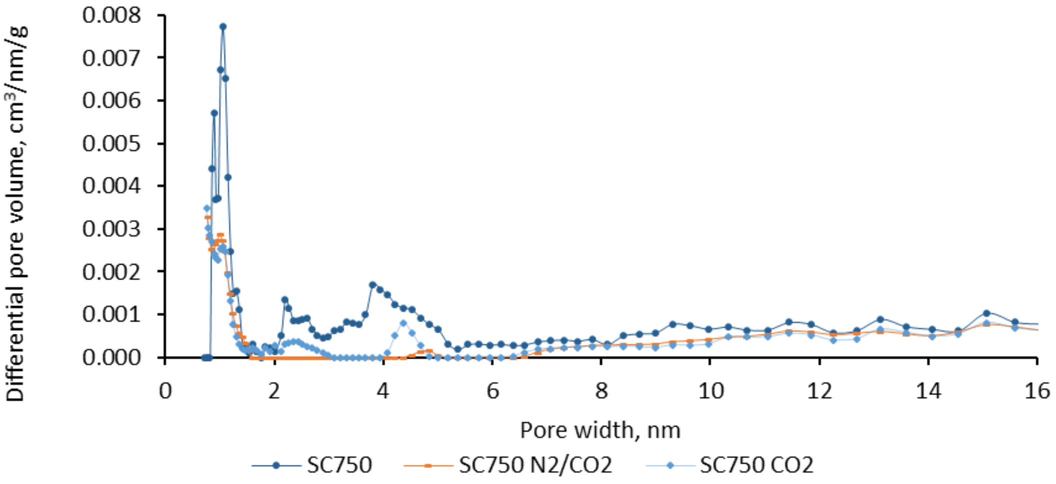


Figure 5: Pore size distribution of semi-cokes prepared in three different atmospheres: 100 % N_2, 50/50 % N_2/CO_2, 100 % CO_2

4. Conclusions

The aim of this research was to study the effect of thermal treatment on oil shale semi-coke. Surface characteristics of semi-cokes prepared using different temperatures and atmospheres were studied. The results showed that when raising the temperature from 550 °C to 900 °C in N_2 environment, surface area increased from 12.5 to 31.3 m^2/g. Higher temperatures promoted the release of volatiles from pores and created more complex porous surface. Although an increase in microporosity was also noticed, the materials were still considered as meso- and macroporous. The effect of CO_2 in the pyrolysis environment was also studied. Instead of promoting the development of porous structure the surface area decreased noticeably, from 24.0 to 13.0 m^2/g. According to the results, the best surface characteristics were obtained at higher temperatures in N_2 environment.

Acknowledgements

This work was supported by the Estonian Research Council grant (PSG266).

References

Bai J., Wang Q., Jiao G., 2012, Study on the pore structure of oil shale during low-temperature pyrolysis, Energy Procedia, 17, 1689–1696.

Borrego A.G., Garavaglia L., Kalkreuth W.D., 2009, Characteristics of high heating rate biomass chars prepared under N_2 and CO_2 atmospheres, International Journal of Coal Geology, 77, 409–415.

Dupre K., Ryan E.M., Suleimenov A., Goldfarb J.L., 2018, Experimental and computational demonstration of a low-temperature waste to by-product conversion of U.S. oil shale semi-coke to a flue gas sorbent, Energies, 11, 3195–3210.

Gao S.P., Zhao J.T., Wang Z.Q., Wang J.F., Fang Y.T., Huang J.J., 2013, Effect of CO_2 on pyrolysis behaviors of lignite, Journal of Fuel Chemistry and Technology, 41, 257–264.

Guo W., Yang Q., Sun Y., Xu S., Kang S., Lai C., Guo M., 2020, Characteristics of low temperature co-current oxidizing pyrolysis of Huadian oil shale, Journal of Analytical and Applied Pyrolysis, 146, 104759.

Han X., Jiang X., Yan J., Liu J., 2011, Effects of retorting factors on combustion properties of shale char. 2. Pore structure, Energy and Fuels, 25, 97–102.

Han X., Jiang X., Yu L., Cui Z., 2006, Change of pore structure of oil shale particles during combustion. Part 1. Evolution mechanism, Energy and Fuels, 20, 2408–2412.

Han X., Külaots I., Jiang X., Suuberg E.M., 2014, Review of oil shale semicoke and its combustion utilization, Fuel, 126, 143–161.

Konist A., Järvik O., Pihu T., Neshumayev D., 2018, Combustion as a possible solution to pyrolytic wastewater utilization, Chemical Engineering Transactions, 70, 859–864.

Loo L., Maaten B., Siirde A., Pihu T., Konist A., 2015, Experimental analysis of the combustion characteristics of Estonian oil shale in air and oxy-fuel atmospheres, Fuel Processing Technology, 134, 317–324.

Luo Y., Ben H., Wu Z., Nie K., Han G., Jiang W., 2019, Impact of CO_2 on pyrolysis products of bituminous coal and platanus sawdust, Polymers, 11, 1–12.

Maaten B., Järvik O., Pihl O., Konist A., Siirde A., 2020, Oil shale pyrolysis products and the fate of sulphur, Oil Shale, 37, 51–69.

Nassef E., Eltaweel Y., 2019, Removal of zinc from aqueous solution using activated oil shale, Journal of Chemistry, 2019, 1–9.

Neshumayev D., Pihu T., Siirde A., Järvik O., Konist A., 2019, Solid heat carrier oil shale retorting technology with integrated CFB technology, Oil Shale, 36, 99–113.

Pihu T., Konist A., Puura E., Liira M., Kirsimäe K., 2019, Properties and environmental impact of oil shale ash landfills, Oil Shale, 36, 257–270.

Rajeshwar K., 1981, The kinetics of the thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry, Thermochimica Acta, 45, 253–263.

Sing K.S.W., 1985, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure and Applied Chemistry, 57, 603–619.

Valdés C.F., Betancur Y., López D., Gómez C.A., Chejne F., 2018, Effects of pyrolysis atmosphere on the porous structure and reactivity of chars from middle and high rank coals, Ingenieria e Investigacion, 38, 31–45.