DISTRIBUTION OF ORGANIC AND INORGANIC INGREDIENTS IN ESTONIAN OIL SHALE SEMICOKE

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At oil production in vertical retorts large amounts of a solid retorting residue – semicoke – are formed and stored in ash piles. Producing activated carbon could be one possibility for utilizing residual carbon present in semicoke. A series of experiments with some semicoke samples accompanied by their SEM and EDAX analysis was carried out in order to elucidate the distribution of carbon and mineral part in semicoke and to estimate the bonding between organic and mineral matter as well as possibilities for their separation for subsequent enrichment. The distribution of key elements in Estonian oil shale semicoke particles was characterized, and the possibilities for carbon extraction were analyzed. The effect of additional thermal treatment of semicoke samples was estimated, and preliminary separation tests using selective grinding were carried out.

Introduction

Estonian oil shale is utilized mainly as fuel for electricity production, a minor part (about 1.5 t per year) [1] is used as a raw material for producing shale oil. At oil production in vertical retorts large amounts of a solid residue – semicoke (approx. 0.6 t/t) are formed which are stored in ash piles (about 100 million tonnes up to now). Due to the presence of several toxic compounds like water-soluble phenols, sulphide sulphur, PAH, etc., the semicoke is a source of severe environment pollution and is classified as a dangerous waste. High and progressively growing waste taxes would cause economical problems in oil production in the near future.

During the last years more attention has been paid to utilizing the remaining energetic potential of semicoke, for example, burning it at the place of formation in a specially built boiler [2–7]. One possibility for

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utilizing the residual carbon of semicoke could be its treatment to obtain activated carbon. Getting activated carbon from fly ashes has been studied by several authors who showed that the residual carbon extracted from ashes is an excellent precursor for obtaining activated carbon [8–10]. Because of the increase in the consumption of activated carbon on the annual level of about 7%, related to its rising usage especially in environment protection and industry, the new sources for its production are welcome.

Therefore, the goal of the present research was to estimate whether the residual carbon in oil shale semicoke could be used to obtain this valuable product. To reach this goal it is essential to determine the distribution of carbon and mineral part in semicoke particles, to estimate the bonding between organic and mineral matter and possibilities for their separation. Further treatment includes enrichment in carbon using mechanical sieving, froth flotation, gravitation, electrostatic or other methods. Also, the changes in semicoke mineral matter, especially those of Ca compounds, during thermal treatment were the objects of the present research.

Materials and Methods

Semicoke samples SC-1, SC-2 and SC-4 (Table 1) were taken from vertical retorts (1,000 t per day) of *AS Viru Keemia Grupp* (Viru Chemistry Group Ltd.) at different times – in 1995, 1998 and 2001, respectively.

Table 1. **Characterization of the Semicoke Samples**

	SC-2	SC-4	SC-1	SC-1, 700
Content, % (dry basis):				
A^d	73.9	69.5	68.4	69.5
Organic matter	12.0	10.5	17.3	10.5
CO_2^M	14.3	20.0	14.4	15.5
C	14.4	15.2	18.24	13.45
S	2.87	2.46	2.24	2.10
N	0.05	0.05	0.05	0.05
H	0.79	0.33	1.39	0.20
CaO_{free}	0.84	0.70	0.85	2.76
Particle size, mm	0–5	0–5	1–5	1–5
SSA, m^2/g	2.98	1.93	1.56	8.29

Distribution of elements in oil shale and its semicoke samples was characterized by SEM and EDAX analysis methods. Additional thermal treatment of semicoke was carried out in a laboratory electric tube heater or muffle-furnace in the atmosphere of N_2 or N_2–CO_2. In addition, BET specific surface area (SSA) measurements were performed using nitrogen adsorption method. Preliminary tests for selective grinding were carried out in a laboratory-scale equipment [11]. For SEM and EDAX analysis semicoke 8–10-mm particles were used. In order to follow possible changes in element mapping and structure, some semicoke samples were heated at 600 °C for 1 hour to complete the devolatilization and at 700 °C for 1 hour (sample SC-1, 700) in order to achieve, in addition to devolatilization, also partial decomposition of carbonates.

SEM photo (100×)   Ca (100×)

C (100×)   Si (100×)

C (1000×)   Si (1000×)

Fig. 1. SEM photo of the SC-4 particle: distribution of Ca, C and Si over the cross-section area of the particle (magnification given in brackets)

SEM photo   Ca

Si   C
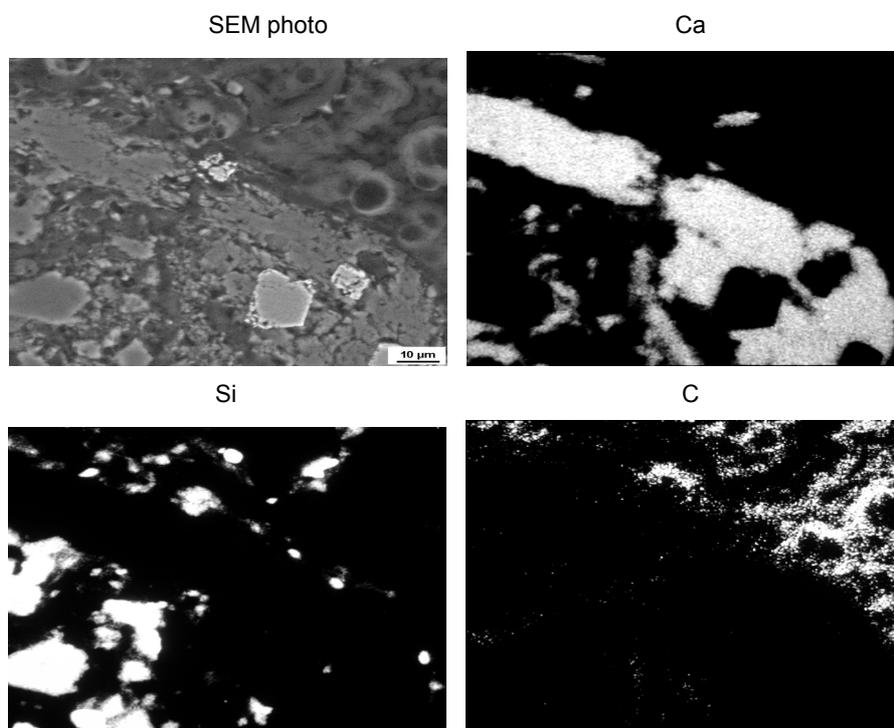
Fig. 2. Distribution of Ca, Si, and C over the cross-section area of the SC-2 particle heated at 600 °C (magnification 100×)

Results and Discussion

When using the residual carbon of fly ashes, the ordinary first stadium in activated carbon production – separation of volatile matter – can be avoided, because pyrolysis has already occurred during combustion and only activation of carbon is necessary. Compared with coal ashes, oil shale semi-coke has both similar and essentially different properties. Their residual carbon content is similar, also most of their volatile matter has emitted. Some characteristics are different: content of volatiles, distribution of carbon and its form (organic matter or coke), bonding with the mineral part, etc.

It can be seen in Table 1 that organic matter content in the samples studied is noticeably low, and additional thermal treatment of SC-1 at 700 °C decreased it by 40% (13.5% of residual carbon). The ash content is extremely high, and it is evident that without enrichment or separation of carbon (coke) from the mineral part, realization of the process of subsequent activation of carbon will not be successful.

Si (SC-4)

K (SC-4)

Al (OS)

K (OS)

Fe (SC-4)

S (SC-4)
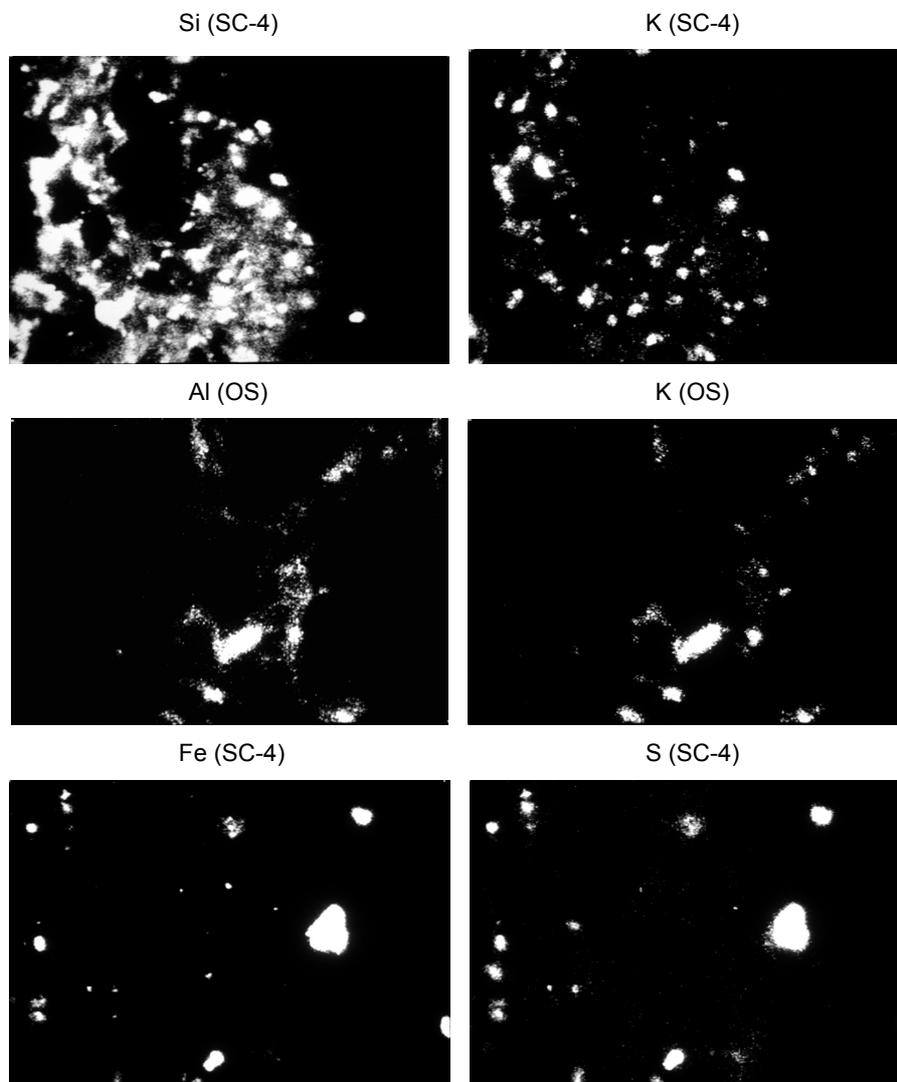
Fig. 3. Distribution of Si, K, Al, Fe and S over the cross-section area of the particles of SC-4 and OS (magnification 1000×)
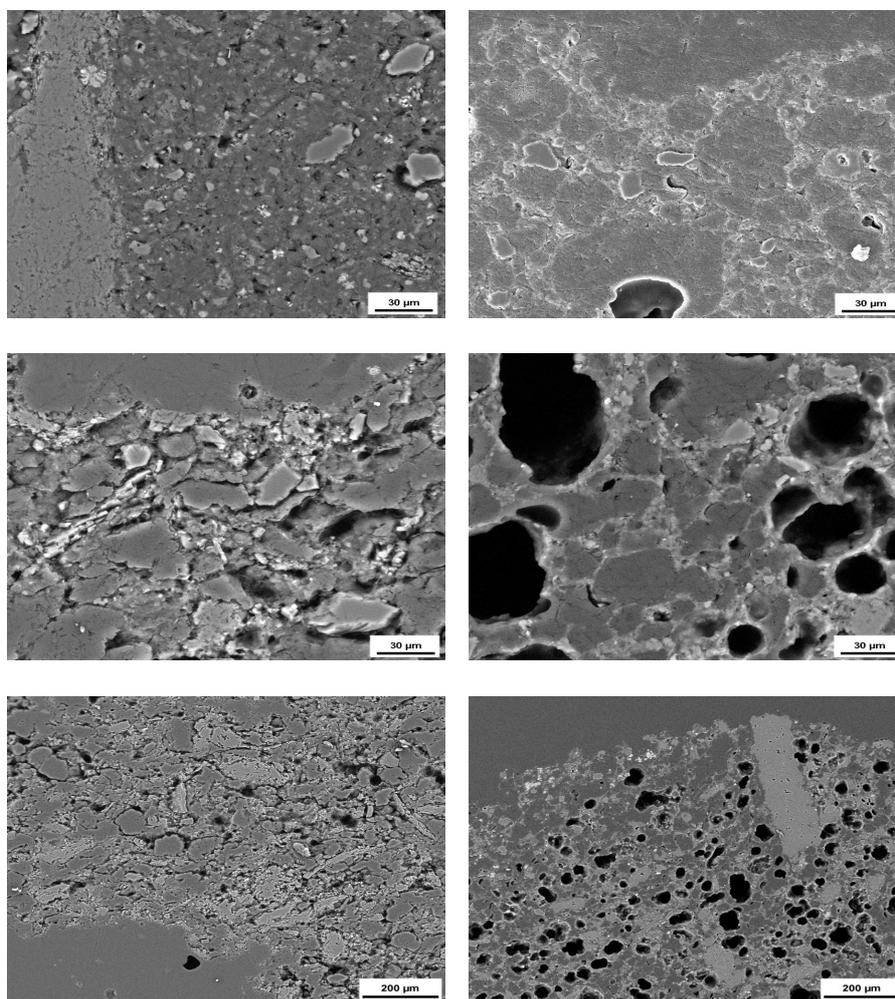
Fig. 4. SEM photos of SC-4: left column – initial sample particles, right column – particles heated at 600 °C

EDAX analysis of the cross section of the oil shale sample particle shows that Ca distribution over the cross section is compact; calcium carbonate is not dispersed in the organic part having sharp borders with surrounding matter. The same is also correct for the heated semicoke samples (Fig. 1). In some particles, Si and C were distributed in the adjacent regions, but this is not the case for all the samples studied (Fig. 2). When using bigger magnification, one can see that Si compounds form more compact formations and C is more finely divided between the Si areas. K locations on the particle cross section partly coincide with the Si areas (Fig. 3), but also with Al which indicates the presence of clay minerals – various aluminium potassium silicates. Also the locations of Fe and S coincide, which indicates

the presence of pyrite, and on some photos the pyrite particles can be well distinguished (Fig. 3).

So, on the basis of SEM and EDAX analysis it can be presumed that calcium compounds (calcium carbonate and some calcium oxide formed at heating) as well as pyritic part could be easily separated from carbon or coke in order to enrich the semicoke. Clay minerals and other silicates are in some cases quite scattered in the organic part, so making the separation of Si-containing compounds from the organic matter more difficult.

Additional heating at 600 °C did not affect visibly the boundaries between organic and mineral parts. However, formation of a new phase around the ingredient particles can be distinguished (Fig. 4). The SSA of heated semicoke SC-1 was about 5 times higher as compared to the initial semicoke sample. This can be explained by the growth of porosity of organic matter as can be seen in Fig. 4, but also by the growth of porosity due to partial decomposition of $CaCO_3$ indicated by the increase in the CaO_{free} content of SC-1 at heating (see Table 1). So, most likely the new phase formed around the particles at heating is calcium oxide. This should favor separation of these ingredients during grinding and enrichment and concentrating of CaO as separate particles.

Table 2. **Fractional Composition, %, of SC-4 Heated at 700 °C for 1 Hour and Ground at Different Speeds**

Fraction, mm	Sieve analysis			A^d			Organic matter		
	Grinding speed, m/s								
	16.5	30	54	16.5	30	54	16.5	30	54
+0.63	50.00	38.60	8.98	77.02	78.31	78.46	8.24	8.37	7.62
+0.4	11.62	12.32	6.73	78.94	77.33	77.48	4.49	6.60	5.87
+0.16	12.65	13.76	13.06	78.00	77.00	76.95	5.10	4.68	6.62
+0.1	5.80	7.80	11.02	79.44	78.00	77.02	3.46	5.38	4.95
+0.071	2.08	3.08	5.72	78.83	78.87	77.09	6.70	3.79	4.71
+0.045	4.15	6.16	11.02	80.58	80.40	78.40	5.26	4.60	4.55
−0.045	13.70	18.28	43.47	86.00	85.36	84.18	5.26	5.44	5.22

Fraction, mm	CO_2^M			CaO_{free}		
	Grinding speed, m/s					
	16.5	30	54	16.5	30	54
+0.63	14.74	13.32	13.92	3.20	3.22	2.52
+0.4	16.57	16.07	16.65			
+0.16	16.90	18.32	16.43			
+0.1	17.10	16.62	18.03	3.64	4.38	2.52
+0.071	14.47	17.34	18.20			
+0.045	14.16	15.00	17.05			
−0.045	8.74	9.20	10.60	4.30	4.23	3.50

Separation tests, including grinding in centrifugal mill and sieving, were carried out at three different grinding speeds: 16.5, 30 and 54 m/s. The results are presented in Table 2. It can be seen that increasing grinding speed decreased the yield of the fraction +0.63 mm from 50 to 9% and increased the yield of fine fraction (–0.045 mm) as well as of the fractions 0.045–0.071 and 0.1–0.16 mm.

Ash content of all the fractions is similar, being slightly higher in the finest fractions. Organic matter content is slightly higher in the coarse fraction, but the differences are insignificant. CaO content is only slightly higher in the finest fraction, which is in correlation with the conclusions made on the basis of SEM analysis. Carbonates are distributed evenly in all the fractions studied and their content of the finest fraction increases very slowly with grinding speed.
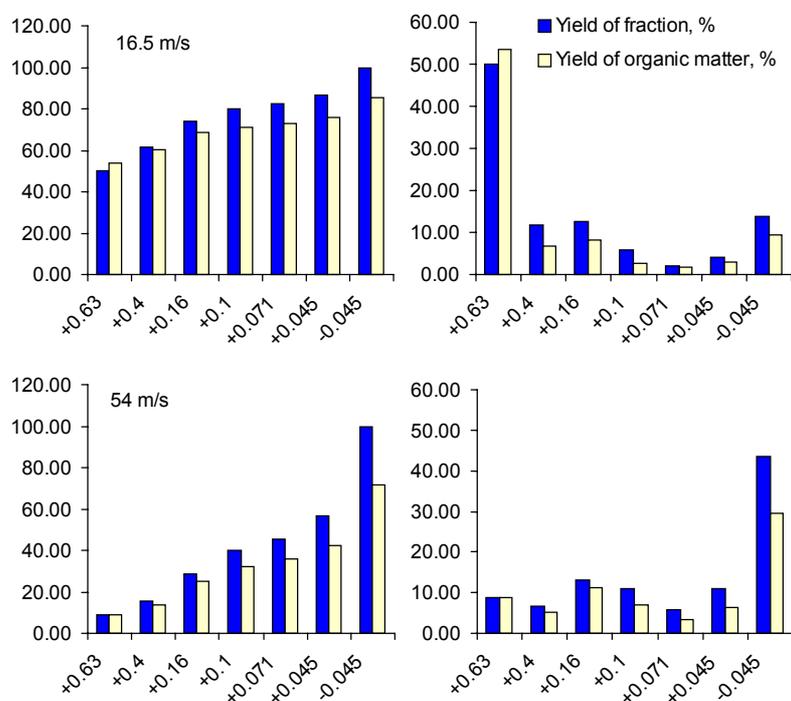
Fig. 5. Cumulative (left) and absolute (right) yield of organic matter in different fractions of semicoke at grinding speed 16.5 and 54 m/s

Conclusions

- The distribution of key elements in Estonian oil shale semicoke particles was characterized using SEM and EDAX analysis methods and the possibilities for extracting carbon from semicoke were studied.

- The existence of sharp borders between limestone particles and other constituents of semicoke was shown. The particles of pyrite and quartz are also located in the material distinguishably.
- The most dispersed ingredient in semicoke is clay.
- The effect of additional thermal treatment of semicoke samples was estimated, and preliminary separation tests using selective grinding were carried out. It was found that selective grinding and sieving do not give increased carbon content in any of the selected fractions; so, more complex separation methods for extraction of carbon from semicoke should be used.

Acknowledgements

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