

Characterization of Chinese, American and Estonian oil shale semicokes and their sorptive potential

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ABSTRACT

The primary byproduct of current oil shale oil extraction processes is semicoke. Its landfill deposition presents a potential threat to the environment and represents a waste of a potentially useable byproduct. Here we examine the sorptive characteristics of oil shale semicoke. Oil shale samples from Estonia, China and the United States were pyrolyzed at 500 and 1000 °C and their products analyzed for organic char content, surface area and porosity. Pyrolysis of the oil shales at temperatures of 500–1000 °C yields semicokes with organic char contents from 1.7% to 17.5% and BET surface areas of 4.4–57 m² g⁻¹, corresponding to 100–550 m² g⁻¹ of organic char. For comparison, the BET surface areas of class F coal fly ashes (combustion byproducts of bituminous coals) typically range from 2 to 5 m² g⁻¹, corresponding to 30–60 m² g⁻¹ of carbon while class C fly ash (from low rank coals) have carbon BET surface areas comparable to oil shale semicoke organic char surface areas.

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1. Introduction

Oil shale, a fine-grained sedimentary rock, often contains a proportionally large amount of kerogen, which can be converted into oil by thermal degradation. Worldwide deposits of oil in shale are estimated at 2.8 trillion barrels of recoverable oil, which is a conservative figure given that oil shale resources from some countries are not reported or the deposits are not fully investigated [1]. The world's largest oil shale deposits are found in Australia, China and the United States, though currently only Israel, Russia, Germany, Brazil, Estonia and China utilize their reserves. In some scenarios, the economics of oil production from oil shale may hinge upon finding suitable and environmentally acceptable uses of the semicoke byproduct of the retorting process.

Today, the byproduct of oil shale production, semicoke, finds commercial use as an aggregate in asphalts, in construction bricks, in cements, as a soil amendment, in rock wool insulation, chemicals, rubber softeners, sulfur, ammonia and power generation, among others [2,3]. However, the total use of oil shale byproducts in these various products represents only a small fraction of the oil shale semicoke produced each year. In addition there is a potential for a large increase in the production of semicoke byproduct if oil production from shale oil were to increase. Currently, the majority of semicoke is disposed of in landfills, and concern about large volumes of byproduct disposal is a major factor used to argue against greater development of this resource.

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Based on the WEC 2007 report, Estonia was the world's largest producer of shale oil, producing 345,000 ton of shale oil per year. Approximately 8000 ton of shale oil was utilized for domestic electricity generation; 98,000 ton of oil for heat generation and the remaining 222,000 was exported [1]. In Estonia the solid semicoke byproduct of shale oil production is mostly disposed of in open dumps; currently approximately 300 million ton of solid semicoke waste is present in such dumps.

The placement of oil shale semicoke into open dumps presents a potential threat of groundwater pollution by polycyclic aromatic hydrocarbons, heavy metals and phenols via leaching from the semicoke by rain and snow that some suggest are entrained in the semicoke waste [4,5]. Such dumping of oil shale semicoke presents a hazard that evokes images like the recent breach of a coal fly ash containment pond in Harriman, TN, USA, releasing an estimated 5.4 million cubic yards of slurry in what some called "the largest environmental disaster of its kind in the United States" [6].

Previous studies by Manor et al. [7], Stout et al. [8], Trikkel et al. [9] show that the organic char content of oil shale semicoke is relatively high, reaching up to 20 wt.%. The organic char in oil shale semicoke does not exist as pure carbon, but rather a carbon system with residual hydrogen and other heteroatoms [7,10]. The Estonian oil shale organic char C/H mass ratio is reported to be as high as 8 [10]. At this point, we clarify that hereafter we use term "char" to refer to only the organic portion of the oil shale coke, and when we use the term "semicoke" we refer to the organic plus inorganic portions of the oil production byproduct.

The relatively high organic matter (char) content in oil shale semicoke leads to a relatively high surface area; the surface area

of Pakistani oil shale semicoke is reported to be $21 \text{ m}^2 \text{ g}^{-1}$ [11]. Moreover, Dogan and Uysal [12] report Turkish spent oil shale surface areas in the range from 19 to $117 \text{ m}^2 \text{ g}^{-1}$ of spent shale with the exception of Himmetoglu spent oil shale sample pyrolyzed at 700°C , which is reported to have a surface area as high as $183 \text{ m}^2 \text{ g}^{-1}$. As a comparison, the BET surface area of a typical class F fly ash (coal combustion byproduct) with a carbon content of about 6 wt.% is as high as $5 \text{ m}^2 \text{ g}^{-1}$ fly ash [13–15].

A scant amount of the oil shale literature focuses on the characterization of oil shale semicokes, and even less investigates specifically the semicoke organic char. Rather the majority of the literature focuses on the oil shale retorting process, quantifying extractable oil, and general characteristics of the oil derived from shale. Without defining the sorption characteristics of spent oil shales Taulbee et al. [2] suggested that the most likely use for oil shale semicokes could potentially be industrial emissions control systems to remove NO_x , SO_2 , NH_3 , H_2S and aqueous pollutants such as phenols. To our knowledge there has been no systematic study of the organic char content, surface area and pore-size distribution of oil shale semicokes. Therefore, the motivation behind this work is to investigate these characteristics of various oil shale semicoke samples pyrolyzed at 500 and 1000°C . The oil shale samples investigated herein were obtained from three continents, in order to see if there were any geographical trends in the results.

2. Experimental

2.1. Materials

Three oil shale samples were obtained from the Maoming mine in the Guangdong province of southwest China, with the local Chinese classification (or grade) of A–C. One sample was obtained from the Huadian mine in the Jilin province of northeast China (grade C oil shale). There were three samples from Green River, Colorado (USA), and one sample from the Aidu mine in northeast Estonia. All eight oil shale samples examined in this work were ground and sieved to yield samples with a particle size between 45 and $75 \mu\text{m}$.

In the pyrolytic sample preparation, approximately 5 g of each oil shale was placed into a porcelain crucible, which was inserted into a laboratory tube furnace maintained at two temperatures, 500 and 1000°C , under a helium flow of 300 mL min^{-1} . The mass loss in the 500°C pyrolysis experiments is attributed mostly to the removal of volatile matter (kerogen), and to the lesser extent the water removal. The mass loss in the 1000°C pyrolysis experiments is attributed to the removal of volatile matter (kerogen), then to the decomposition of calcite and dolomite in the mineral portion of the shale and to the lesser extent the water removal.

Oil shale mass loss between the temperatures of 120 and 500°C was ascribed to the pyrolytic mass loss from kerogen. Fischer Assay oil yield, in units of gallons of oil per ton of oil shale (GPT), was estimated from kerogen content of the shales according to Cook [16], but was also given by the sample providers in a few cases.

2.2. Oil shale organic char content

A TA Instruments thermogravimetric analyzer (TGA) model 951 enabled determination of organic char contents of the oil shale semicoke samples prepared in the above pyrolysis process. Approximately 5–10 mg of sample was placed on a platinum pan in the TGA. The sample was heated to 120°C at a rate of $30^\circ\text{C min}^{-1}$ and held for 20 min to remove physically adsorbed water, after which the sample was heated at $20^\circ\text{C min}^{-1}$ to 600°C and held for 35 min to determine the loss of the organic portion of the semicoke. Each sample was analyzed at least three

times to ensure reproducibility. It is worth mentioning that we did not see any water in the semicokes, since our samples were stored in air-tight jars to mitigate atmospheric exposure following their pyrolytic preparation. At temperatures above 620°C the weight loss from oil shale semicokes is likely due to decomposition of carbonate materials such as calcite, dolomite and ankerite, and should be separately accounted for when the char content of oil shales is measured [11].

2.3. Surface area and porosity characterization

The porous character of the semicokes was examined employing the standard volumetric N_2 adsorption technique. Here we use a fully automatic Quantachrome Corp. Autosorb-1 system. Depending upon the approximate surface area of the sample, 100–500 mg of oil shale semicoke powder was placed into a sample vial and out-gassed at 300°C overnight to clean the surface of the sample. The isotherms were obtained by recording the N_2 adsorption/desorption data points at relative pressures from 10^{-6} to 1. These adsorption data points were used to calculate the Brunauer, Emmett and Teller (BET) surface areas and the porosities of each of the oil shale semicoke samples [17,18]. The BET surface area of the semicoke was determined over the partial pressure (P/P_0) range where the BET equation had the highest correlation coefficient. For most samples having little microporosity, the commonly accepted partial pressure range to determine BET surface area is 0.05–0.3. For slightly microporous samples, the isotherms' relative pressure range for BET area determination requires adjustment. In this work, with slightly microporous oil shale semicoke samples, the BET areas were determined at significantly lower P/P_0 values, in the range of 0.03–0.1, as suggested by Gregg and Sing [18].

The pore sizes discussed in this work are reported according to IUPAC classification, which defines micropores as pores of width less than 20 \AA , pores in the range of $20\text{--}500 \text{ \AA}$ as mesopores and pores above 500 \AA as macropores. Micropore volumes of the oil shale semicoke samples were determined by applying the Dubinin–Radushkevitch (DR) model to N_2 adsorption isotherms [18]. The mesoporosity of the oil shale semicoke samples was determined by subtracting the DR microporosity value (in mL per gram of semicoke) from the porosity value (in mL per gram of semicoke), determined at an isotherm relative pressure, P/P_0 , of 0.95. The macroporosity of the semicoke sample was determined by subtracting the porosity value at a relative pressure $P/P_0 = 0.95$ (in mL per gram of semicoke) from the porosity value at a relative pressure $P/P_0 = 0.99$ (in mL per gram of semicoke). The specific porosities of the oil shale organic chars were calculated by dividing the semicoke porosities by the organic fraction present in oil shale semicokes.

The pore-size distributions of oil shale semicokes were determined from the nitrogen adsorption isotherms at 77 K using Density Functional Theory (DFT) [19,20]. The SEM images of oil shale semicokes were taken to qualitatively further investigate porosity using a LEO 1530 VP ultra high resolution Field Emission Scanning Electron Microscope (FE-SEM).

3. Results and discussion

3.1. Oil shale oil yields

The oil shales studied have Fischer Assay values ranging from 21 to 77 GPT (see Table 1). The Estonian oil shale had the highest value of 77 GPT, whereas the three Colorado oil shale samples had estimated Fischer Assays of 21, 27 and 51 GPT and those compared well to values provided by the oil shale supplier (see Table 1).

Table 1
Fisher assay oil yields, oil shale semicoke organic char content, BET surface areas and porosity values of the oil shale semicoke and organic char for eight samples studied.

Sample name	Fisher assay (GPT)	Pyrol. temp. (°C)	Organic char (wt.%)	BET area (m ² g ⁻¹) (coke)	BET area (m ² g ⁻¹) (char)	Micro-porosity (mL g ⁻¹) (char)	Meso-porosity (mL g ⁻¹) (char)	Macro-porosity (mL g ⁻¹) (char)
Chinese A	45	500	17.3	57.0	306	0.117	0.322	0.650
Maoming		1000	11.4	43.5	341	0.149	0.184	0.386
Chinese B	47	500	17.5	52.9	278	0.109	0.267	0.650
Maoming		1000	9.7	33.7	299	0.133	0.500	1.265
Chinese C	38	500	8.0	34.4	370	0.150	0.673	1.546
Maoming		1000	4.7	30.9	552	0.255	0.915	2.830
Chinese	37	500	8.3	35.6	373	0.145	0.653	1.596
Huadian		1000	4.2	19.9	355	0.189	0.898	2.128
Estonian	77	500	9.1	33.4	332	0.132	0.115	0.100
		1000	7.9	40.3	468	0.164	0.493	0.708
Col. 50 GPT	51	500	6.2	23.0	338	0.175	0.099	1.195
		1000	2.1	9.9	362	0.147	0.454	0.812
Col. 25 GPT	27	500	3.4	14.7	372	ND	ND	ND
		1000	2.2	4.2	94	ND	ND	ND
Col. 19 GPT	21	500	2.6	10.0	301	ND	ND	ND
		1000	1.7	4.4	136	ND	ND	ND
Typical coal class F ash	NA	NA	3.4	2.6	57	0.046	0.021	0.077
Typical coal class C ash	NA	NA	0.7	3.1	326	0.091	0.137	0.046

NA, not applicable; ND, not determined.

These are in agreement with commonly reported values for such shales such as those given by Miknis et al. [21]. The Chinese oil shale samples have Fischer Assay values ranging from 37 to 47 GPT. The Chinese Maoming mine oil shales A and B are somewhat similar with slightly higher Fischer Assay results as compared to the Chinese Maoming sample C and the Huadian oil shale sample, which are more mineral-rich samples.

3.2. Organic char in oil shale semicokes

The organic char contents in all oil shale semicoke samples are moderately high, ranging from 1.7 to 17.5 wt.% (see Table 1) with the Chinese and Estonian oil shale samples having the highest organic char contents. These data agree well with results presented in the literature [7–9]. The difficulties associated with measuring the organic char content in oil shale semicoke (as in any mineral-rich matter, coal fly ash included), is related to defining, explicitly, the true mass loss in the TGA associated with combustion of organic matter. Loss-On-Ignition (LOI) tests [13–15], widely used on coal combustion products, cannot be applied without modifications on oil shale semicoke samples pyrolyzed at temperatures lower than 850 °C. The calcite and dolomite-rich oil shale semicokes, when pyrolyzed at temperatures lower than 850 °C, could still contain un-decomposed carbonate in their semicoke products, which will readily decompose when exposed to temperatures of 620 °C and above in oxidation experiments [11]. This can clearly result an overestimation of the oil shale semicoke organic char content. Keeping this in mind, we oxidized our 500 °C pyrolyzed oil shale semicoke samples at maximum 600 °C temperature in the TGA. We believe that at this temperature, most of the organic matter is lost, and the rate of decomposition of calcite and dolomite is low enough so as to not impact the organic matter content determination. However, we have determined that the 1 h 1000 °C in helium flow pyrolyzed oil shale samples have their calcite and dolomite portions completely decomposed, and would have no effect on the organic portion determination in TGA.

The amount of organic matter in oil shale semicoke clearly decreases with the increase of pyrolysis temperature (see Table 1). This trend suggests that not all the organic matter in the low temperature semicoke is pure carbon, but rather, retains some hydrocarbon character. The presence of carbonates can also support CO₂ self-gasification of chars in oil shale semicokes as the pyrolysis temperature increases [7].

As we expected, the percent organic char of Chinese oil shale sample A decreased from 17 wt.% to about 11 wt.% when the pyrolysis temperature was increased from 500 to 1000 °C, and for Chinese sample B we observed a slightly larger decrease in organic char content, from 17 to 10 wt.%. For the Huadian sample the organic content decreased from 8 to 4 wt.%, and for Maoming sample C, from 8 to 5 wt.%. The lower values in the latter two cases had to do with the lower amount of organic matter in the starting oil shales. In general, for all oil shale semicokes there is a loss of about a third of the remaining organic matter when the pyrolysis temperature is increased from 500 to 1000 °C.

For comparison with the oil shale semicokes, a class F coal combustion fly ash typically has a carbon content of up to 6 wt.% when combusted under normal boiler conditions, whereas the carbon content in class C coal fly ash is typically as low as 1 wt.% [14]. The organic content of oil shale ashes, obtained from PF systems, are in order of magnitude lower: less than 0.3% in bottom ash and less than 0.03% in fly ash [10]. The oil shale semicoke organic char content is significantly higher than that in these combustion byproducts, which are of course very different types of materials. These char contents are offered as a basis of comparisons for the discussion below.

3.3. Surface area and porosity distribution in oil shale semicokes

There is a great deal of information about the adsorption capacity of various sorbents available from the raw adsorption isotherms. Fig. 1 presents the N₂ adsorption isotherms of the Estonian oil shale semicoke pyrolyzed at 500 and 1000 °C. The oil shale semicoke isotherms are compared to class F coal fly ash isotherms. Clearly, the oil shale semicoke adsorption capacities are significantly higher than the coal fly ash adsorption capacity, due to the higher organic content of the oil shale semicoke. Oil shale semicoke isotherms are somewhat close to type II isotherms except that the oil shale semicoke isotherms exhibit a steep rise at relative pressures below 0.1 (typically characteristic of type I isotherm). This is an indicator of the presence of micropores [18]. The steady rise of the oil shale semicoke isotherm between relative pressures of 0.1 and 0.95 supports the existence of a large network of mesopores. The adsorption isotherm's further increase, beyond a relative pressure of 0.95, is attributed to the macroporosity of the sample. The N₂ isotherms on Fig. 1 are not normalized on the basis of organic matter, but instead offered as per gram or whole semicoke and fly ash. Even

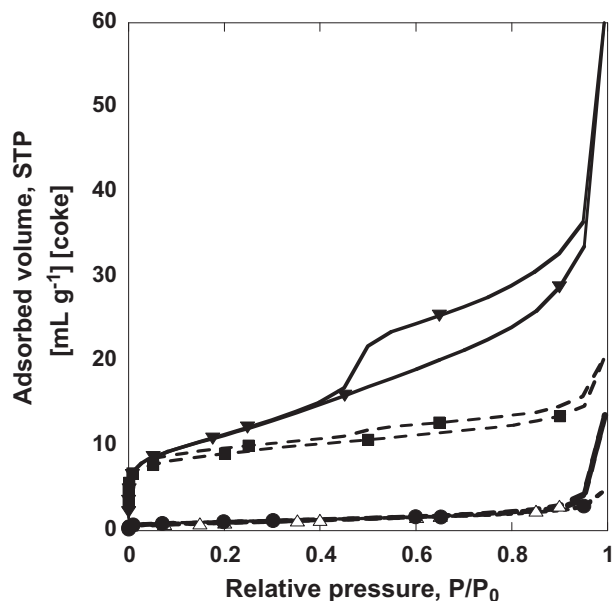


Fig. 1. Nitrogen adsorption isotherms of oil Estonian oil shale semicokes pyrolyzed at 500 and 1000 °C, compared to typical coal class F and C fly ash isotherms. ■: Estonian oil shale semicoke, 500 °C; ▼: Estonian oil shale semicoke, 1000 °C; △: Estonian oil shale semicoke inorganic portion; ●: Class F coal fly ash.

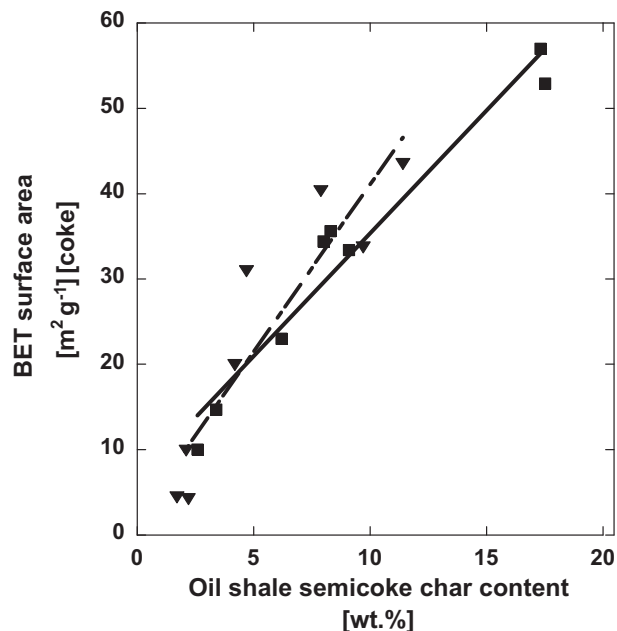


Fig. 2. Oil shale semicoke BET surface areas vs their organic char content for samples pyrolyzed at 500 °C and 1000 °C. ■: Pyrolyzed at 500 °C; ▼: Pyrolyzed at 1000 °C.

without the isotherm normalization, it can be concluded that the adsorption capacity is significantly higher for the Estonian oil shale semicoke sample pyrolyzed at 1000 °C, compared to the adsorption uptake of the same oil shale semicoke pyrolyzed at 500 °C. The difference of the slopes of both isotherms (semicoke pyrolyzed at 500 and 1000 °C) is most prominent at a relative pressure range of 0.1–0.95, suggesting the presence of the wide range of mesopores in the semicoke sample pyrolyzed at 1000 °C.

The BET surface areas of all oil shale semicokes ranged from 4.4 to 57 m² g⁻¹ of semicoke, which is agreement with the results available in literature [11,12], except for the single Dogan and Uysal [12] reported 183 m² g⁻¹ of area value. Unfortunately Dogan and Uysal [12] did not report what the organic char content of this particular 700 °C spent oil shale sample was, but it must have been high to support such a high surface area per gram of semicoke.

Not surprisingly, there appears to be a clear correlation between the BET surface areas of our oil shale semicokes and their organic char contents, shown in Fig. 2. This is expected, as most surface area resides in the organic char of the oil shale semicoke.

The organic char contents, together with pure mineral BET surface area values of the oil shale semicokes, were used to calculate the specific surface areas of the oil shale semicoke chars as summarized in Table 1. The BET surface areas of the pure mineral part of the oil shale semicokes were determined to be 2–5 m² g⁻¹, compared to that for a typical coal fly ash mineral surface area of 0.8 m² g⁻¹ [14]. Specifically, the BET surface area of the mineral content of the Estonian oil shale was 3.5 m² g⁻¹, for the three Colorado shales an average of 2.2 m² g⁻¹, and for the Chinese shales the BET mineral surface area was an average of 5.1 m² g⁻¹. The higher surface area of the oil shale mineral portion is believed to be due to the particles' morphologies, which are irregular and not uniform, as are the minerals in the fly ash samples. The class F coal mineral ash contains mostly uniform glassy particles, which have undergone a melt phase in the boiler, since they have seen temperatures well above their fusion temperatures (well above 1000 °C). The slightly different morphologies of the retorting semicoke minerals and the fly ash minerals are clearly visible in the SEM micrographs of Fig. 3A and B.

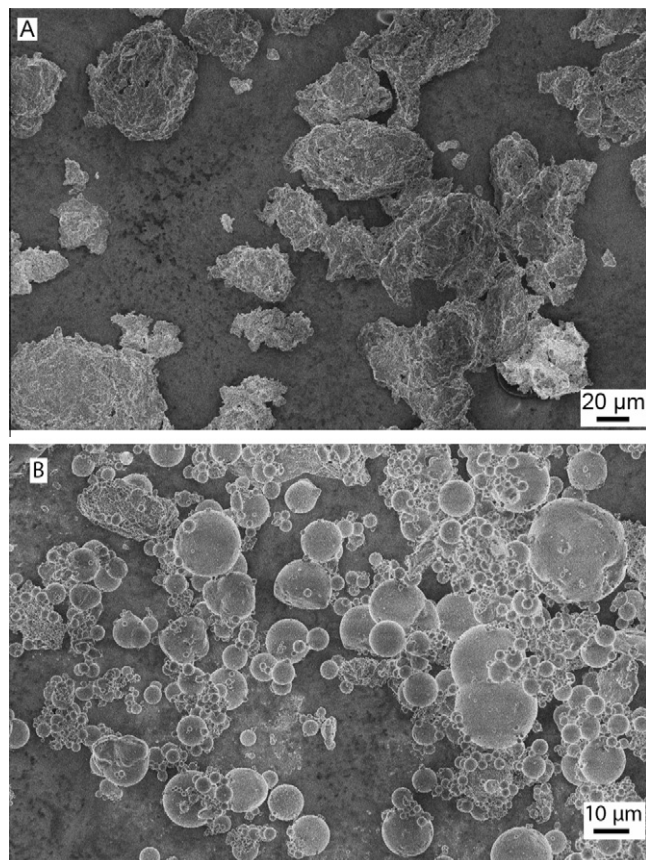


Fig. 3. SEM images of Estonian oil shale semicoke mineral matter after oxidation at 750 °C for 2 h (A), and class F coal fly ash mineral matter after oxidation at 750 °C for 2 h (B).

The BET surface areas of the oil shale organic chars ranged from 100 to 550 m² g⁻¹ (see Table 1), which is an order of magnitude

higher than those for class F fly ash chars (usually in the range of 30–60 m² g⁻¹). The oil shale char BET areas are, however, comparable to class C coal fly ash char surface areas [14]. The difference between the class F and class C fly ash carbons arises from the fact that the organic matter of the former passes through a melt phase during pyrolysis, whereas the organic matter of the latter does not. It is not clear whether this is the reason for a high surface area in the case of the oil shale char. In this case, the kerogen clearly produces copious amounts of oil, which normally is not characteristic of heavy cross-linking of the whole of the organic content. On the other hand, this does not necessarily mean that what remains, as the char did not undergo cross-linking before it could pass through a melt phase.

To our knowledge, these are the highest specific BET surface areas of oil shale semicoke organic char thus far reported. Akar and Ekinçi [3] reported that the specific surface area of steam activated oil shale char is 400 m² g⁻¹ of organic char. Yet, we see similar and indeed higher surface areas without any activation of the oil shale semicoke char. The high specific BET surface area is present in all oil shale semicoke organic chars tested, and seems to be independent of the origin of the parent oil shale. There is no clear trend of the organic char BET surface area with the pyrolysis temperature (see Table 1). However, analysis of organic char porosity sheds further light on this matter.

Dogan and Uysal [12] and Derbyshire et al. [22] have reported that the macroporosity of the spent oil shale semicoke increases linearly with the pyrolysis temperature from 400 to 700 °C. In addition, Dogan and Uysal [12] suggests that the macroporosity is the source of the reported high oil shale semicoke surface area (the one up to 183 m² g⁻¹). However, it seems highly unlikely that only macropores can support such a high surface of the semicoke. In our work, independent of the origin of oil shale, the largest volumes of pores in the oil shale semicoke organic char are found in meso- and macropores (see Table 1). In several of the cases shown in Table 1, significant increases in macropores are observed at the same time that surface areas decrease, showing that it cannot be the macropores that determine the surface area. Both micro- and mesoporosity of the oil shale organic char generally increase with pyrolysis temperature, but again, Table 1 shows that the relationship of this increase to surface area is not always clearly visible. It is, however, the case that the oil shale semicoke char BET surface area is best correlated with the char micropore volume (see Fig. 4). The complexity of the relationship between micro- and mesopore volumes and surface area is best understood by looking further to the actual pore-size distributions. It is clear that because there is such a broad range of sizes involved in mesopores, their contributions to surface area can vary widely; depending upon what size range the mesopores fall into.

Figs. 5 and 6 show the results of DFT pore-size distribution analysis on Estonian oil shale, Chinese A and Colorado Green River 50 GPT semicoke pyrolyzed at 500 and 1000 °C together with typical class F and C coal fly ash carbon data. The results in Fig. 5 clearly indicate that there is a large decrease of micropores less than <8 Å, and the growth of micropores near 16 Å with the increase of pyrolysis temperature. In addition, there is a significant growth of mesopores between 26 and 45 Å with the increase of pyrolysis temperature. This trend seems to be independent of the origin of the parent oil shale, as seen in Fig. 6 (here plotted as a cumulative distribution for greater clarity). This mesopore increase with pyrolysis temperature might well be attributable to CO₂ self-gasification of the char in the pyrolysis procedures at 1000 °C, as seen also by others [7]. If this is the case, then the oil shale semicoke chars at higher temperature have the ability to 'self-activate' through the carbon–CO₂ gasification reaction. The source of the CO₂ in this self-gasification process, whether from the organics or

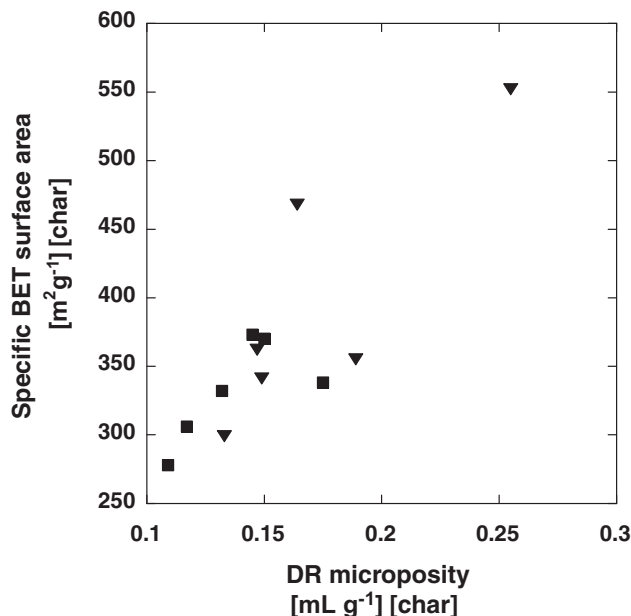


Fig. 4. Specific BET area vs DR microporosity of semicoke organic chars for samples pyrolyzed at 500 and 1000 °C. ■: Pyrolyzed at 500 °C; ▼: Pyrolyzed at 1000 °C.

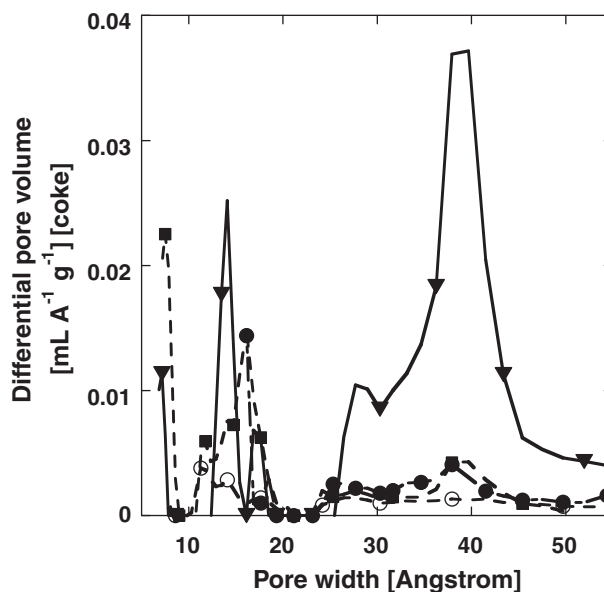


Fig. 5. DFT/Monte-Carlo differential pore volume distribution of Estonian oil shale semicoke pyrolyzed at 500 and 1000 °C, and of a typical class F coal fly ash. ■: Estonian oil shale semicoke char, 500 °C; ▼: Estonian oil shale semicoke char, 1000 °C; ●: Class F coal fly ash char; ○: Class C coal fly ash char.

from a decomposition of calcite at higher pyrolysis temperatures, is not immediately clear.

Scanning Electron Microscope (SEM) images of Estonian oil shale semicokes pyrolyzed at 500 and 1000 °C are presented in Fig. 7. The particles exhibit high macroporosity and show little evidence of fusion. Most particles have an irregular shape and are an average size of 40–50 μm. No major differences in the porous nature of the two semicokes pyrolyzed at 500 and 1000 °C were observed in the SEM images. For comparison with oil shale chars, a typical class F coal fly ash carbon offers much lower micro- and mesoporosity. On the other hand, a typical class C coal ash char shows comparable microporosity (in pores <16 Å). The 500 °C oil

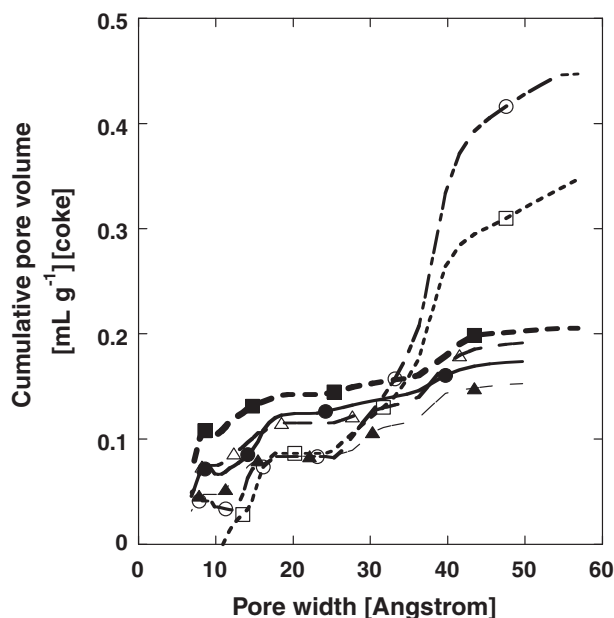


Fig. 6. DFT/Monte-Carlo cumulative pore volume distribution of Estonian, Colorado 50 GPT and Chinese A oil shale semicoke chars pyrolyzed at 500 and 1000 °C. ●: Estonian, 500 °C; ○: Estonian, 1000 °C; ■: Colorado 50 GPT, 500 °C; □: Colorado 50 GPT, 1000 °C; ▲: Chinese A, 500 °C; △: Chinese A, 1000 °C.

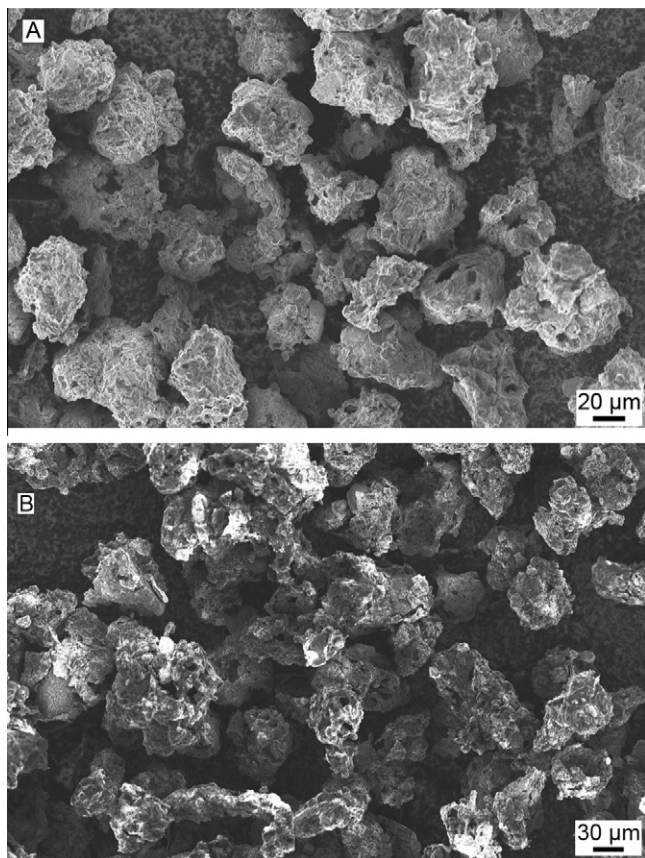


Fig. 7. SEM images of Estonian oil shale semicoke (A) pyrolyzed at 500 °C (B) pyrolyzed at 1000 °C.

shale semicoke char micropore volumes are very similar to the class C coal fly ash carbon micropore volumes (Table 1).

3.4. Waste to byproduct conversion: Sorbent capacity of oil shale semicoke

As discussed in the introduction to this work, the relatively high char content and high organic char surface areas and porosities of oil shale semicokes offer a potential to utilize these materials as sorbents. This is a relatively new concept, with only a handful of studies that explore the feasibility of utilizing the solid waste of oil shale retorting. Trikkel et al. [9] believed that without separation of the char and mineral part the materials would be unattractive. They attempted to extract carbon from semicoke *via* grinding and screening, pneumoseparation and triboelectrodeposition. They concluded “none of the methods used gave promising results in getting carbon rich products from semicoke suitable for producing activated carbon” [9]. Some suggest there is a relatively high particle-bound content of polycyclic aromatic hydrocarbons, phenols and other oil products to semicokes; this characteristic exemplifies the ability of this waste material to sorb pollutants [4]. Here the challenge is to ensure that the chars are either “clean” of such residual materials or will not release them, if they are to be used as a sorbent. If the fraction of material to be used as a sorbent were exposed to the higher temperatures studied here, then it is unlikely that any of the potentially extractable organics would survive on the surface.

Shawabkeh et al. [23,24] use Jordanian oil shale combustion ash treated with either nitric acid or sodium hydroxide to remove copper and zinc ions from aqueous solution, so this class of materials is attracting increasing attention for such applications.

The work presented here on the relatively high sorptive capacity of these oil shale semicokes opens further lines of research into the reactivity of such chars and whether or not they are useable as sorbents given compounds such as PAH, phenols and trace metals that may be entrained within the semicokes. Research is ongoing to determine the amount of PAH-s, phenols and trace metals if present in these semicokes to gauge the feasibility of direct usage or pretreatment to remove entrained compounds. However, given the drive to develop alternative fuel sources, the ability to convert the copious amounts of semicoke waste from the retorting process for use as a sorbent makes oil shale an increasingly viable source of energy by decreasing its environmental impact and increasing economic incentives.

4. Conclusions

The investigation into the characteristics of eight oil shale semicokes from China, Estonia and the United States, each pyrolyzed at two temperatures, show a moderately high surface area carbonaceous char in quantities sufficient for it to be of interest as a potential sorbent. The amount of char in oil shale semicoke depends on processing conditions and parent shale. Interestingly, it is not necessarily a richer oil content oil shale that yields more char in its semicoke. The specific BET surface area of the oil shale semicoke organic char is comparable to class C coal fly ash, yet there is considerably more organic matter available in the oil shale semicoke (up to 17 wt.%) than in class C coal fly ash (up to 1 wt.%), and may not require any additional activation.

Our results suggest the existence of a high volume in the oil shale semicoke pyrolyzed at 1000 °C, wide range mesopore network leading into micropores, where the majority of the surface area is located. This trend seems to be independent of the origin of the parent oil shale. Oil shale semicoke’s relatively high char content and wide range of network of mesopores makes a strong initial argument for the use of this material as a sorbent to mitigate the environmental threat that the current dumping of this waste product poses.

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