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Improving the Environmental and Economic Viability of U.S. Oil Shale via Waste-to-Byproduct Conversion of Semicoke to Sorbents

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Supporting Information

ABSTRACT: This investigation demonstrates the feasibility of mitigating the economic and environmental burdens associated with commercialization of oil shale by converting its primary solid waste, semicoke, to an adsorbent material. U.S. White River Mine oil shale was pyrolyzed at 600 °C to produce a semicoke; its activation energy of pyrolysis was calculated using the distributed activation energy model to be 206.9 kJ/mol, similar to other domestic oil shales. This simulated semicoke was chemically activated using HCl, KOH, and a double-activation procedure of either HCl followed by KOH or vice versa. The acid-activation step was considerably more effective in developing the surface area and porous network of the semicoke sorbents, as well as removing carbonate minerals, than KOH. The activation energies of oxidation of the raw, pyrolyzed, and activated samples ranged from 100.5 kJ/mol (raw) to 189.0 kJ/mol (semicoke), with the activated samples between these values. Of the activated samples, HCl + KOH had the lowest overall average oxidation-activation energy, 104.4 kJ/mol, and also had the highest derivative thermogravimetric curve peak, indicating high reactivity. The BET surface area of this sample was 74.3 m²/g. However, in the interest of reducing process steps, the single activation using HCl is likely a more efficient option for byproduct conversion, yielding a BET surface area of $51.7 \text{ m}^2/\text{g}$, which is considerably higher than that of Class F coal fly ash, at $\sim 5\text{m}^2/\text{g}$, a waste material that is commonly employed as a sorbent.

1. INTRODUCTION

Over the past several decades, concerns over dwindling fossil fuel resources prompted a surge in research and development of alternative energy technologies, including oil shale, an unconventional fossil fuel. Oil shale is a fine-grained sedimentary rock that contains from 100 to 200 L/(metric ton) of organic matter, known as kerogen.¹ The organic matter can be converted into oil by thermal degradation of the compacted rock. It is estimated that there are upward of 409 billion tons of shale oil *in situ* (2.8 trillion U.S. barrels of shale oil) in the U.S., primarily located in the Eocene Green River Formation of the Piceance and Uinta Basins in Colorado and Utah.^{1,2}

To date, the only commercially viable approach to obtain energy from oil shale is via the mining and surface processing of the rock. The primary byproduct of oil extraction via *ex situ* retorting is semicoke, a semicarbonaceous material that can be burned or cofired as a low-value, high-ash energy source, or used as low-value construction additives, all of which represent only a small fraction of the semicoke produced worldwide each year.^{3,4} Recently, groups have begun extracting alumina-silicates and other ceramics from oil shale ashes,^{5,6} which still leaves the semicarbonaceous system behind. In Estonia, where 98% of the country's electricity comes from oil shale, semicoke and ash piles dot the landscape,⁷ representing a threat to the environment and, in the case of semicoke, a waste of organic material. The U.S. Geological Survey (USGS) cites the disposal of large quantities of spent shale, as well as the potential for leaching of organic and inorganic pollutants from such piles contaminating surface and ground waters, as two of the potential primary environmental impacts of the oil shale industry.² This explanation was given as early as the 1970s for the lack of development of this alternative fossil fuel.⁸ Yet, potential exists for this waste material to be transformed into high-value byproducts, improving the economic and environmental viability of oil shale as an unconventional hydrocarbon source.⁹

Prior studies show a relatively high organic content of semicoke (up to 20 wt %); it exists as a carbonaceous system with residual hydrogen and heteroatoms.^{10–12} Semicoke has relatively high surface areas (up to 117 m²/g of spent shale) and oxidative reactivities as compared to coal fly ash.^{10,11,13} Oil shale ash (resulting from complete oxidation) was shown to be a proficient adsorbent to remove pesticides from aqueous solution.¹⁴ Jordanian oil shale semicoke, activated with CO₂, KOH, and ZnCl₂, has been shown to remove phenol from aqueous solutions.¹⁵ However, given the relatively high concentrations of polycyclic aromatic hydrocarbons¹⁶ and heavy metals¹⁷ present in semicoke, its use for aqueous phase adsorption or as a soil amendment without treatment is

Received: September 28, 2015 Revised: November 25, 2015

questionable. However, much potential remains for flue gas treatment, especially if the surface area of the material can be further increased. Taulbee et al. suggested that a semicoke sorbent would be useful in removing NO_x, SO₂, NH₃, and H₂S in industrial emissions controls.³ Since many oil shales are rich in carbonate minerals, they have the potential to adsorb large quantities of SO₂ without the addition of CaO or limestone normally required to control sulfur emissions.¹⁸ Furthermore, Tiikma et al. demonstrated the ability to fix chlorine evolved from the pyrolysis of mixed plastic wastes containing polyvinyl chloride onto Kukersite oil shale, its semicoke, and its ash.¹⁹ Prior work suggests that semicokes pyrolyzed at 500 °C from China, Estonia, and the United States show surface areas high enough to be of use as an industrial sorbent, similar to and higher than that of coal fly ashes.¹⁰ Ichcho et al. chemically activated Moroccan oil shale using weight ratios of H₃PO₄:oil shale of 0.25 to 2, pyrolyzed at 250 and 450 °C for between 1 and 3 h. Resulting BET surface areas ranged from 47 to $315 \text{ m}^2/\text{g}^{20}$ However, the sample used in their work was raw oil shale pretreated with hydrocholoric acid and dried, though not pyrolyzed or combusted, so the direct comparison with this work-which focuses on waste-to-byproduct conversion of semicoke-is difficult to make. Others have demonstrated the ability to chemically modify the surface of raw oil shale and oil fly ash (resulting from firing of liquid oil) to improve their capacities as sorbent materials.^{21,22} This has yet to be demonstrated for oil shale semicokes, and specifically for reserves from the United States.

The proposed waste-to-byproduct conversion of oil shale semicoke is motivated by both fiscal and environmental concerns. With advances in mining, retorting, and especially upgrading techniques, the price of recovering oil from oil shale in the United States has dropped precipitously over the past decade. Domestic companies predict that, at current production costs, oil from oil shale is profitable when oil is selling for as low as \$40 (U.S.) per barrel; the 52 week NYMEX high/low for crude oil are \$96.72 and \$48.71/barrel, respectively. However, the cost of production versus the price of crude oil remains one of the primary roadblocks to widespread U.S. market development. By creating value-added byproducts, we can improve the economic viability of oil shale processing. In addition, the environmental implications of widespread semicoke disposal are dire; the production of oil shale semicoke and ash has irrevocably altered the Estonian landscape and damaged the aqueous and subsurface environments. The two primary issues are water contamination from heavy metals and organics entrained in the semicoke and resculpting the landscape with semicoke "mountains" that could possibly collapse and harm humans, as we recently saw in the U.S. with coal fly ash containment collapses, or catch fire as in a recent landfill fire in Kukruse, Estonia. It is for these reasons that the U.S. and other countries such as Russia, China, and Brazil are reluctant to explore their own vast reserves. However, by removing the need to dispose of the oil shale semicoke, we remove yet another barrier to the widespread use of oil from oil shale. In addition, by using semicoke, a waste material, as a sorbent for flue gas treatment, we further improve the environmental nature of flue gas cleaning, as many sorbents are manufactured from raw, rather than waste, materials.

2. EXPERIMENTAL SECTION

2.1. Semicoke Preparation. The oil shale used in this work was collected from the White River Mine, Utah, USA, a part of the

Mahogany zone mining horizon, one of the richest sections of oil shale in the Green River Formation, with average Fisher assay of 25–35 GPT.²³ The Mahogany zone is identified by the USGS as a primary target for development because of its enhanced kerogen content, rich in lipid materials with predominantly aliphatic chains and also the thickness of deposits and limited overburden.^{24,25} Various rock samples were ground and sieved to a particle size < 125 μ m. Samples were loaded in porcelain crucibles and placed in a 1 in. Lindberg MightyMite tube furnace. Samples were pyrolyzed in high-purity nitrogen at 100 ± 5 mL/min (measured via an Omega flowmeter) subjected to a heating rate of 10 °C/min, held at 110 °C for 30 min, then heated to a final temperature of 600 °C, and held for 60 min to produce the "semicoke". Samples were cooled under nitrogen to room temperature before being removed to prevent oxidation.

2.2. Chemical Activation of Semicoke. To chemically activate the semicoke samples, 1 ± 0.005 g of semicoke was combined with an equal mass of either HCl or KOH and 50 mL of deionized water, covered, and stirred for 17 h at room temperature. While these extreme conditions (mass ratio and time) may not be immediately industrially applicable, our aim is to demonstrate a viable pathway with the largest possible conversions. The samples were vacuum filtered and dried, then heated in a furnace under high-purity nitrogen at a rate of ~20 °C/min, held at 600 °C for 60 min, and allowed to cool to room temperature. In the case of a double activation (HCl followed by KOH, or vice versa), the aforementioned procedure was repeated with the second activating reagent. Acid treatment is known to remove mineral matter while retaining organic matter from unconventional fuels such as oil shale and asphaltites; such treatment is often suggested as a precursor to pyrolysis to improve volatile product evolution.²

2.3. Physical Characterization of Raw Materials and Sorbent Samples. The carbon content of the sorbent materials was determined using a Mettler-Toledo TGA-DSC-1. Mass is recorded every second to the 10^{-8} g, along with temperature to ± 0.1 K. No more than 10 mg was used in each experiment to minimize potential transport limitations within the crucible. Reactive gas (nitrogen or air) is fed from the gas flow controller at a rate of 50 mL/min, with a protective balance nitrogen flow of an additional 20 mL/min. Samples were placed in a 70 μ L alumina cruicible. Total carbon was determined as the loss upon heating in air to 910 °C; volatile carbon (that available for adsorption) was determined via heating to 610 °C in nitrogen as mineral carbonates decompose after ~620 °C.²⁷

A fully automated Quantachrome sorption apparatus was used to measure nitrogen adsorption isotherms to describe the surface area and porosities of the oil shale semicokes. Approximately 150–450 mg of each sample was loaded into 6 mm sample tubes; pre- and postdegassing weight was measured on a Sartorius semi-microbalance to ± 0.1 mg. Samples were degassed at 180 °C for at least 12 hours. BET surface areas of the semicoke sorbents were determined over the partial pressure (P/P_0) range between 0.05 and 0.3; adjustments to slightly lower P/P_0 values, as suggested by Gregg and Sing, were made when appropriate for slightly microporous samples.²⁸

A Rigaku MiniFlex powder X-ray diffractometer (XRD) was used to assess relative changes in mineral composition upon activation of the semicoke samples.^{29,30} Relevant instrument conditions are Cu-anode tube, 30 kV/(15 mA), 0.03 degree steps, and 0.7 s count time per step.

2.4. Kinetics of Raw Material and Sorbent Samples. To compare the relative reactivity and energy required to extract oil from this oil shale sample to its worldwide counterparts, we determined the activation energy of pyrolysis of the raw shale. It was pyrolyzed in high-purity nitrogen in the Mettler Toledo TGA/DSC-1. The sample was heated to 110 °C and held for 30 min to ensure moisture removal. The temperature was ramped back down to 25 °C at -10 °C/min and held for 5 min. Then the sample was heated at 10, 20, or 50 °C/min up to 900 °C and held for 60 min to obtain a stable mass reading. Less than 10 mg of sample was used for each experiment to minimize potential transport limitations within the crucible, filling the crucible approximately 2 mm high (crucible height is 5.1 mm). Ollero et al. have shown, using the same TGA, that by limiting internal diffusion effects (which appeared with char sample heights greater than 3 mm)

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Table 1. Activation Energy of Pyrolysis of Raw White River Mine Oil Shale Calculated via the Distributed Activation Energy Model (R^2 at Conversion at 0.55 and 0.60 < 0.99 and Therefore Omitted)

mass fraction converted	E (kJ/mol)	$A(s^{-1})$
0.10	162.9 ± 10.2	$1.28 \times 10^8 \pm 6.04$
0.15	171.2 ± 11.6	$2.57 \times 10^8 \pm 7.42$
0.20	180.7 ± 9.9	$7.91 \times 10^8 \pm 5.31$
0.25	181.0 ± 11.7	$5.63 \times 10^8 \pm 7.13$
0.30	187.3 ± 11.3	$1.14 \times 10^9 \pm 6.56$
0.35	189.7 ± 14.3	$1.22 \times 10^9 \pm 1.04 \times 10$
0.40	199.6 ± 11.3	$4.58 \times 10^9 \pm 6.24$
0.45	205.0 ± 12.8	$7.75 \times 10^9 \pm 7.86$
0.50	219.1 ± 14.9	$4.91 \times 10^{10} \pm 1.07 \times 10$
0.65	306.4 ± 21.6	$2.64 \times 10^{12} \pm 1.59 \times 10$
0.70	242.5 ± 32.9	$2.90 \times 10^8 \pm 6.06 \times 10$
0.75	224.1 ± 33.9	$1.80 \times 10^7 \pm 6.38 \times 10^7$
0.80	217.1 ± 34.0	$5.32 \times 10^6 \pm 6.12 \times 10^6$
0.85	209.4 ± 36.4	$1.54 \times 10^6 \pm 7.87 \times 10$
av	206.9 ± 10.4	$1.94 \times 10^{11} \pm 2.75 \times 10^{11}$

Table 2. Comparison of Pyrolysis-Activation Energies ofRaw Oil Shale Across the Literature

oil shale	E (kJ/mol)	ref
El-Lajjun, Jordan	4.7-68.0	36
El-Lajjun, Jordan	7.0-68.4	37
Sultani, Jordan	8.0-63.6	37
Mengen, Turkey	21.8-33.4	38
Timhadit Site, Morocco	31.6-90.4	39
Green River Shale, Colorado, USA	41-206	40
Çan, Turkey	41.1-57.6	37
Himmetoglu, Turkey	48.6-64.9	37
El-Lajjun, Jordan	75	41
El-Lajjun, Jordan	98-120	42
Mengen, Turkey	131.9-185.3	43
Maoming Shale, China	139.1-286.8	44
Fushun Shale, China	154.8-288.6	44
Puertollano, Cuidad Real, Spain	155	45
Himmetoglu, Turkey	158.6-172.5	43
Anvil Points Shale, Colorado, USA	178.7-218.7	46
Çan, Turkey	182.2	43
White River Mine, Utah, USA	206.9 ± 10.4	this work
Green River Shale, Colorado, USA	209	33
Clear Creek Shale, Colorado, USA	254	47
Anvil Points Shale, Colorado, USA	247	47

the external diffusion effects (both heat and mass) were virtually negligible below 850 $^{\circ}\text{C.}^{31}$

To determine the impact of activation condition on the relative reactivity of each sample, we determined the activation energy of oxidation for each sample. The same temperature profile and heating ramp rates as used for pyrolysis of the raw shale were applied, with the difference being we used 50 mL/min of air as the reactive gas, with 20 mL/min of nitrogen as the balance protective gas. Experiments were performed in accordance with recommendations from the ICTAC on determination of reaction kinetics of solid fuel decomposition.³²

The distributed activation energy model (DAEM) is commonly applied to assess the kinetics of solid fuels' pyrolysis and oxidation, including oil shale.^{33,34} The DAEM assumes that the decomposition of a solid occurs via an infinite number of parallel, irreversible first order reactions, each with different activation energies, *E*, occurring simultaneously. The DAEM assumes that all of the reaction activation

	BET surface area (m ² /g _{char})	specific BET surface area $(m^2/g_{carbon,volatile+fixed})$	micropore surface area (m^2/g)	micropore vol (cm ³ /g)	volatile carbon content (mass frac)	fixed carbon content (mass frac)	ash content (mass frac)	av oxidation-activation energy (kJ/mol)
raw	12.9 ± 0.4	16.7 ± 1.3	14.0 ± 0.4	0.0050 ± 0.0005	0.493 ± 0.025	0.280 ± 0.014	0.227 ± 0.011	100.5 ± 9.5
pyrolyzed	48.4 ± 2.0	222.3 ± 17.8	67.6 ± 2.0	0.0240 ± 0.0022	0.134 ± 0.007	0.084 ± 0.004	0.782 ± 0.039	189.0 ± 7.1
HCl activated	51.7 ± 2.3	327.8 ± 26.2	76.8 ± 2.3	0.0270 ± 0.0024	0.030 ± 0.001	0.128 ± 0.006	0.842 ± 0.042	119.4 ± 3.1
KOH activated	31.2 ± 1.5	132.4 ± 10.6	49.1 ± 1.5	0.0175 ± 0.0016	0.134 ± 0.007	0.102 ± 0.005	0.764 ± 0.038	183.7 ± 27.1
HCl + KOH activated	74.3 ± 3.2	475.4 ± 38.0	106.5 ± 3.2	0.0380 ± 0.0034	0.027 ± 0.001	0.129 ± 0.006	0.844 ± 0.042	104.4 ± 7.8
KOH + HCl activated	95.5 ± 4.1	627.1 ± 50.2	136.3 ± 4.1	0.0485 ± 0.0044	0.029 ± 0.001	0.123 ± 0.006	0.848 ± 0.042	122.7 ± 3.8

Table 3. Surface Area, Carbon Content, and Oxidation Kinetics Analysis of Raw, Pyrolyzed, and Activated Oil Shale Semicokes



Figure 1. Surface area and specific surface area of raw, pyrolyzed, and activated semicokes.



Figure 2. Surface area as a function of carbon content for oil shale samples.

energies have the same preexponential factor, k_0 , at the same mass fractional conversion and that the activation energy has a continuous distribution. The DAEM can be written as

$$X(t) = 1 - \int_0^\infty \exp\left(-A \int_0^t \exp\left(-\frac{E}{RT}\right) dt\right) f(E) dE$$
(1)

where *A* is the frequency (or preexponential) factor, *E* the activation energy, *T* the absolute temperature, and *R* the universal gas constant. X(t) represents the extent of conversion at any time, *t*, calculated by the ratio of the mass of volatiles produced at any given time, equal to the initial mass, m_0 , minus the mass at time *t*, m_v to the total volatiles produced at the end of the pyrolysis reaction, $m_{\rm fr}$.

$$X(t) = \frac{m_0 - m_t}{m_0 - m_f}$$
(2)



Figure 3. XRD results of raw, semicoke, and activated semicoke samples.

f(E) is the distribution of the activation energy, normalized as

$$\int_{0}^{\infty} f(E) \, \mathrm{d}E = 1 \tag{3}$$

If the experiment is conducted nonisothermally at a constant temperature ramp rate $\beta = dT/dt$, eq 1 can be rewritten as

$$X(T) = 1 - \int_0^\infty \exp\left(-\frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT\right)f(E) dE$$
(4)

The frequency factor is often considered a constant for all reactions. However, Miura and Maki allow for a compensation effect between A and E through their integral method applied to the DAEM, as used here.³⁵ The activation energy and frequency factor are determined from TGA curves of at least three discrete heating rates at selected conversion values for different heating rates. As such, the activation energy obtained from the Arrhenius plots of eq 4 are across a range of solid pyrolysis or oxidation decomposition levels. To achieve a 95% confidence in the Arrhenius parameters, if correlation coefficients, R^2 , were below 0.994, additional runs were performed at each ramp rate, and the data added to the plot to ensure this statistical limit, put forth by the ICTAC Kinetics Committee, was met.³² In a few select conversions—likely due to heterogeneity of samples— R^2 were below 0.994 after five sample runs and are thus not included in the overall average activation energy calculation.

3. RESULTS AND DISCUSSION

Presently, the primary stumbling blocks to the commercialization of oil shale as an unconventional fossil fuel are economic limitations and environmental implications. These issues are simultaneous addressed by the proposed process of converting oil shale semicoke, a semicarbonaceous system, to an adsorbent material. For comparison to other shale samples, we first analyzed the activation energies of pyrolysis of raw White River Mine oil shale. Chemically activated semicoke samples were characterized to determine surface area and porosity, changes in mineral matter, carbon content, and oxidation kinetics.

3.1. Pyrolysis Kinetics of Raw Oil Shale. The activation energy of pyrolysis of the raw While River Mine oil shale was determined as a function of fractional conversion using the



Figure 4. SEM images of raw, pyrolyzed, and activated oil shale samples, 20K magnification.

distributed activation energy model, given in Table 1, ranging from 162.9 \pm 10.2 to 306.4 \pm 21.6 kJ/mol. (The isoconversional plot used to determine these energies is available in Figure S1 of the Supporting Information.) The average activation energy calculated from all values with Arrhenius plot correlation coefficients of $R^2 > 0.95$ was 206.9 \pm 10.4 kJ/mol. This is on the higher end of worldwide shale resources, as seen in Table 2, though in excellent accord with other U.S. oil shale samples.

3.2. Impact of Chemical Activation on Oil Shale Semicoke: Physical Characteristics. As seen in Table 3, the White River Mine oil shale semicoke contains 13.4 ± 1.7 wt % volatile carbon, with a BET surface area of almost 50 m²/g_{semicoke}, which is already considerably higher than a typical Class F coal fly ash at only 5 m²/g_{fly ash}, yet fly ash has long been used as sorbent material. The effect of acid treatment on carbonates is well-known; the significant decrease in carbon contents seen for samples treated with HCl is most likely due to the acid dissolving the carbonate minerals present in the oil shale samples. Acid leaching of oil shale is known to increase bitumen extraction, concurrently with carboxylic acids and their salts.⁴⁸ The lower carbon contents and higher average oxidationactivation energies (discussed later) suggest that the acid treatment—though responsible for increasing surface area and porosity—also removes a substantial amount of carbonaceous matter.

Overall, chemical activation had a neutral or positive impact on overall and especially specific surface area, with the exception of the KOH-activated sample. As seen in Figure 1, there was no statistical difference in BET surface area for pyrolyzed versus HCl-activated semicoke (on a per gram semicoke basis), though the KOH-activated semicoke was considerably lower than the other two. The specific surface area (as calculated on a surface area per gram of total carbon, Figure 2) of the HClactivated semicoke was statistically different, though not substantially higher, than the pyrolyzed semicoke. The volatile





b. (\diamond) HCl Activated; (\Box) KOH activated

Figure 5. DTG plots for raw, pyrolyzed, and activated samples oxidized at 10 K/min.

carbon content of the KOH-activated semicoke was the same as the semicoke's content. This, combined with a decrease in surface area, suggests that KOH alone is not an effective chemical-activation technique for oil shale semicokes, despite its widely touted ability to develop micropores in other carbonaceous systems, notably biomasses. 49,50 However. though activation with HCl-and double activation for that matter-results in a considerably lower volatile carbon content, the surface areas are markedly higher than the pyrolyzed sample, with KOH + HCl having the highest surface area, 95.5 \pm 4.1 m²/g. The dual-activation methods increased the micropore volumes of the semicokes considerably; the KOH + HCl sample saw a 2-fold increase in micropore volume, from $0.024 \pm 0.002 \text{ cm}^3/\text{g}$ for the pyrolyzed oil shale to 0.049 cm $^3/\text{g}$ for the KOH + HCl sample and to 0.380 ± 0.003 cm³/g for the HCl + KOH sample. We suspect, from these data alone, that the HCl is responsible for removing a portion of the mineral matter entrained in the semicoke (along with some of the volatile carbon)-but the removal of the minerals leads to increases in porosity.

To determine the impact of treatment on the oil shale semicoke, we turned to XRD analysis; compiled scans of all samples are given in Figure 3, with individual XRD scans available in Figure S2 of the Supporting Information. Upon pyrolysis, we see significant decreases in calcium carbonates (identified as dolomite, $CaMg(CO_3)_2$, and ankerite, $Ca_{1.01}Mg_{0.45}Fe_{0.54}(CO_3)_2$) with some decrease in the albite signals (NaAlSi₃O₈) and virtually no change in quartz (SiO₂). Heat treatment is known to alter minerals within oil shale,⁵¹ as is the ability of HCl to dissolve the carbonate minerals while retaining quartz and clay minerals in (raw) oil shale, as documented by Al-Harahsheh et al.⁵² In this case, the HCl likely attacked the carbonates remaining after pyrolysis, while the basic KOH did not impact these minerals.

Figure 4 presents SEM images taken at 20K magnification using a JEOL JSM-6100 scanning electron microscope. We note more amorphous regions of the raw, semicoke, and KOHactivated samples as compared to the HCl- and doubleactivated samples. These images qualitatively underscore the importance of the acid treatment in removing mineral matter

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and increasing porosity of the semicoke samples to improve the conversion to an adsorbent material.

3.3. Impact of Chemical Activation on Oil Shale Semicoke: Reactivity. Derivative thermogravimetric curves for the five semicoke samples are shown in Figure 5. We note a considerably higher reactivity of the HCl- and double-activated sample, with peak reactivities, dx/dt, of 0.4 wt %/s. The peak reaction rates of the pyrolyzed, HCl + KOH, and KOH samples are roughly equivalent at half of the HCl samples. Furthermore, the raw, pyrolyzed, and KOH-activated samples all show two DTG peaks, the first between 600 and 700 K and the second between 900 and 1000 K, whereas the HCl, HCl + KOH, and KOH + HCl samples show only one peak around 700 K.

Complementary to the DTG data is an analysis of the oxidation-activation energies via the DAEM, presented in Figure 6 for each sample as a function of mass fraction



Figure 6. Activation energy of oxidation for raw, pyrolyzed, and activated samples as determined by the distributed activation energy model: (black dots) raw; (red squares) pyrolyzed; (purple diamonds) HCl activated; (blue triangles) KOH activated; (orange pluses) HCl + KOH activated; (white triangles) KOH + HCl activated.

conversion, with the average activation energy of oxidation given in Table 3. (Table S1 of the Supporting Information presents the activation energy at each conversion level for each sample.) Overall, the activation energies of the pyrolyzed and KOH-activated samples are considerably higher than the raw (expected, given the higher volatile carbon content supporting oxidation^{53,54}) and HCl samples (including the doubleactivation samples). The higher activation energies of the semicoke and KOH-activated samples are attributable to the low volatile carbon and higher carbonate mineral content of the samples, which lead to a higher energy barrier for oxidation than the acid-treated samples. While some have suggested that the residual mineral contents of shale can have a catalytic effect on the oil shale,⁵⁵ the minerals identified by XRD apparently do not catalyze oxidation of the White River Mine semicoke, given the higher activation energies. The increased reactivity of the HCl- and double-activated samples further suggest that they may make suitable adsorbents.¹⁰

The work presented here demonstrates the potential to convert oil shale semicoke, previously know to possess

relatively high reactivities and surface areas, as compared to coal fly ash, to sorbent materials. Such a conversion would mitigate one of the primary environmental impacts of oil shale usage.⁵⁶ Given the desire to decrease the number of process steps and required materials, the most viable chemicalactivation process determined here is the single-step activation using hydrochloric acid. This yielded a potential adsorbent with high reactivity and surface area. Further work on the conversion of processed oil shale is recommended; for example, it has been demonstrated that the composition, morphology and surface area of oil shale ash resulting from pulverized fired versus circulating fluidized bed combustion varies considerably.^{57,58} As such, pyrolysis conditions may also impact the resulting semicoke sorbent's properties. Many energy conversion processes in Estonia today remove limestone present in shale prior to energy recovery;⁵⁹ this would alter the sorbent characteristics and may not be necessary if it is desired to sequester SO_2 in the sorbent. As such, there is likely potential to optimize the sorbent properties of these converted oil shale semicokes based not only on the activation treatment but also in terms of the process used for oil extraction.

4. CONCLUSIONS

This investigation demonstrates the feasibility of mitigating the economic and environmental burdens associated with oil shale semicoke by producing a valuable byproduct. We show that semicoke from U.S. oil shale from the White River Mine can be chemically activated to increase surface area and porosity. The largest BET surface area, of 95.5 \pm 4.1 m²/g (and specific surface area of 627.1 \pm 50.2 m²/g_{carbon}) and micropore volume of 0.485 \pm 0.004 cm³/g were found for the KOH + HCl double-activated semicoke. However, to increase the financial viability of this waste-to-byproduct conversion, by limiting the chemical activation to a single step using HCl, we can achieve a BET surface area of 51.7 \pm 2.3 m²/g (and specific surface area of 327.8 \pm 26.2 m²/g_{carbon}) and micropore volume of 0.270 \pm 0.002 cm³/g. Samples activated with hydrochloric acid (either as a single step or part of a two-step chemical activation) showed decreased carbonate mineral content, higher reactivities in oxygen, and lower activation energies as calculated by the distributed activation energy model.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.Sb02244.

Activation energies of oxidation for the various semicokes, isoconversional plots for activation energy of pyrolysis of raw White River Mine oil shale and for oxidation of raw, semicoke, and activated semicokes, and XRD data plots (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank P. Quinn for providing the oil shale sample and Dr. Joel Sparks of the Boston University Department of Earth and Environment for assistance with XRD measurements. J.X. acknowledges the generous support of the scholarship from China Scholarship Council (CSC) under Grant CSC No. 201406350169. Funding for this work was provided by the Boston University College of Engineering Summer Term Alumni Research Scholars (STARS) Program and the Boston University Undergraduate Research Program (UROP).

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