

DERIVATION OF ADSORBENT CARBONS FROM OIL SHALE RESIDUES

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Introduction

Active adsorbent carbons can be derived from the pyrolysis residues of low-ash oil shales. Besides producing liquid fuels, oil shales, like coal, may be utilized as a source material to produce high-value added products. This utilization also leads to the reduction of waste material.

Oil shale is a sedimentary rock which contains sufficient organic matter (Kerogen) which produces oil and gas when pyrolyzed. In the past, oil shale research has predominantly focussed on maximizing the liquid hydrocarbon yield [1-3]. The primary goal was to produce a substitute for naturally occurring petroleum. These efforts have proven the commercialization of oil shale to be very difficult. Shale oil is simply not, economically, a reasonable substitute for crude oil. Based on current market forces, which suggest the continuation of low crude oil prices and high supply, oil shale commercialization does not appear to be a near-term prospect. To make oil shale more competitive, the development of new high value products needs to be examined.

After pyrolysis, as much as half of the carbon remains in the retorted (spent) shale. This carbon-rich product is generally considered a waste material. Its disposal represents an economic and environmental problem. It is, therefore, important that the pyrolyzed shale be utilized, either in the retorting process as a source of energy, or as a source of new products. The former strategy is the basis for the development of the KENTORT II technology for Eastern US oil shales [4,5]. This technology completely utilizes the carbon on the pyrolyzed shale by incorporating integrated gasification and combustion steps. The latter strategy, the utilization of the spent shale carbon for new products, is the focus of this study.

In previous work it was shown that a range of materials can be manufactured from oil shale residues, including cement and asphalt additives [6,7]. However, the utilization of carbon-rich residues of oil shales as precursor materials for the production of adsorbent carbons has not been examined. The objective of this project is to fabricate adsorbent carbons from low-ash oil shale residues. The production of high-value solids such as adsorbent carbons, in addition to oil, would make the economics of oil shale development more attractive.

Experimental Procedures

Two oil shales from the Turkish Goynuk [8] and the Australian Alpha [9] deposits were selected for this study based on the following criteria: (1) low ash contents and; (2) high oil yields upon retorting. The oil shales were pyrolyzed at 550 °C under a continuous flow of nitrogen. Proximate

and ultimate analyses of the raw and spent shale materials are illustrated in Table 1. The N₂-swept fixed bed pyrolysis experiments were performed in a 1.5 inch stainless steel reactor. The reactor conditions are discussed in detail elsewhere [10]. During pyrolysis, the alginite-rich, low-ash oil shales were observed to form a macroporous network of charred carbonaceous material. Heating stage microscopic (HSM) examination allowed the observation of the spatial relationships between macropores generated by the volatilization of alginite macerals and the char and minerals that stabilize the macrostructure. The HSM apparatus utilized in this study consists of a Zeiss Universal polarized light microscope, a heating stage, and temperature and gas flow controllers.

After pyrolysis, the spent shale was activated in a steam reactor (gasifier) at 880 °C. Water was pumped through a 1/16 inch capillary and entered the reactor below the shale distributor plate, where it is released into the hot zone as superheated steam. The steam passed through the shale zone and exits the reactor, where it is condensed.

Surface area measurements were performed on the samples to investigate porosity development resulting from both the pyrolysis and steam retorting processes. Standard nitrogen adsorption using a static volumetric flow process was used, employing an Autosorb-6 sorption system at a temperature of 77 °Kelvin. All surface area measurements were calculated using the standard BET equation [11] between relative pressures of 0.05-0.25. Micropore volume approximations were calculated using the Dubinin-Radushkavich equation [12] over a linear region of the D-R plot. Samples were outgassed under vacuum at a temperature of 200 °C prior to analysis.

Scanning electron microscopic (SEM) examination of the pyrolyzed and steam activated samples, using a Hitachi S-2700 (magnification up to x 10⁴), allowed a comparison of the morphological features.

Samples of the shale carbons were monitored for their gas adsorption characteristics using thermogravimetry/mass spectroscopy (TG-MS). A temperature programmed adsorption/desorption (TPA/D) analysis was performed using H₂S, NH₃ and NO gases as adsorbates.

Results and Discussion

Pyrolysis Induced Porosity

The pyrolysis induced porosity (PIP) in the retorted shale corresponds to a BET surface area of only 8 - 10 m²/g for both shales (Table 2). However, this framework provides excellent accessibility for steam to infiltrate the chars at 880 °C during activation. The HSM experiments showed that the bulk of the macropores formed when alginite macerals volatilized. These large elongated macropores are inherited from the structure of alginite and vitrinite (desmocollonite) macerals (Figure 1). The temperature at which constituents boiled in these macerals occurred in the HSM experiments at 467 °C. The extensive macroporosity of the carbon-rich pyrolysis residues (from Goyruk and Alpha) indicates these shales to be promising precursors for adsorbent carbons. This is based on the abundant macropores in the chars contributing to an intricate infrastructure that readily allows steam and/or catalyst metals to infiltrate. The action of steam is expected to cause extensive micropore development in the chars. The validity of this working hypothesis was examined by enhancing the inherent porosity (PIP) by catalyzed and uncatalyzed steam treatments at 880 °C.

Steam Induced Porosity

The purpose of the pyrolysis experiments was to provide spent (pyrolyzed) shale for steam activation experiments. The steam induced porosity (SIP) was generated using run times from one to ten hours. The SEM study of the steam treated chars revealed a much rougher surface compared to the pyrolyzed char (Figure 2). The increase in microporosity was documented by the substantial increase in BET surface area of the steam treated samples (Table 2). The SIP was more pronounced after mineral matter removal by acid treatment. This was probably due to the removal of minerals blocking pore entrances. Studies of the effects of steam retorting the spent shale showed that the overall surface area could be increased up to 110 fold by retorting under extremely slow steam flow conditions for prolonged periods of time (up to 10 hours). However this resulted in an extensive loss of carbon. Steam activation at 880 °C for four hours, using steam flow rates of 2 grams/minute, developed a BET surface area of around 400 m²/g with a 43% loss of carbon (Table 2). An inverse relationship was observed between overall surface area and carbon yield from the retort. The percent carbon loss and the relatively high mesopore volumes of the carbons may be dependent on the high reactivity of the shale precursors, or the presence of finely dispersed mineral matter, both of which has yet to be determined. Preliminary studies on the effects of catalytic metals (ZnCl₂; CaCl₂) finely dispersed on the shale surface during activation indicated some improvement over simple steam activation (Table 2).

Adsorbent Carbons from Oil Shale Precursors

Samples of the carbons from shale precursors were monitored for their gas adsorption characteristics using TG-MS. Both the Goynuk and Alpha derived carbons showed higher adsorptive capacities for H₂S and SO₂ than a commercially available carbon. The TPA/D profile for the steam activated Goynuk sample using H₂S as adsorbate indicated the adsorption capacity of the Goynuk carbon material at 70 °C was 0.06 g/g of carbon. The adsorption capacity was based on the weight gain during adsorption, weight loss during desorption, and the identification of H₂S as the only desorbed gas (Figure 3). Samples of shale-derived carbon also demonstrated significant adsorptive capacity for NO and NH₃ (Figure 4), indicating potential uses of shale derived adsorbents as industrial gas scrubber carbons.

Synopsis

Adsorbent carbons can be produced from the pyrolysis residues of the Turkish Goynuk and Australian Alpha oil shale samples. Both materials have low ash contents and produce high oil yields upon retorting at 550 °C. During pyrolysis, a macroporous network of charred carbonaceous material forms. The development of the pyrolysis induced pores (PIP), and that of the macrostructure stabilizing char and mineral matter, were observed using a heating stage microscope. The PIP in the retorted shale corresponds to a BET surface area of only about 10 m²/g, but provides sufficient access for steam to infiltrate the char during activation at 880 °C. The steam induced porosity (SIP) corresponds to a BET surface area of 300-400 m²/g at 43 % burn off. The steam activation treatment results in increased gas adsorption capacities: the Goynuk and Alpha derived carbons showed promising adsorptive capacities for NO, NH₃ and H₂S compared to a commercial carbon. The carbon-rich pyrolysis residues of the two shales under investigation have shown excellent potential as feedstocks for the production of adsorbent carbons. Utilization of the retorted or spent shale can not

only result in new high-value added products, but can also lead to the reduction, and hence regulation, of a waste material.

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Table 1 Ultimate and Proximate Analyses for Goynuk and Alpha

	Goynuk Raw Shale	Goynuk Spent Shale	Alpha Raw Shale	Alpha Spent Shale
C wt%	54.7	49.9	76.6	73.1
H wt%	8.3	1.8	9.9	3.2
N wt%	1.4	1.7	1.1	1.7
S wt%	2.8	2.2	1.3	2.9
Moisture wt%	12.1	3.2	0.9	1.2
Ash wt%	17.2	41.6	4.4	15.6
Volatiles wt%	60.1	16.7	87.7	33.4
Fixed C wt%	10.9	38.2	10.1	49.4
BTU/lb		9150		13400

Table 2 BET - Surface Area Development for Goynuk and Alpha Shales

Sample	BET	BET	BET
		1 h *	4 h **
Goynuk: Pyrolysed	8.8		
Goynuk: Steam Activated		180	350
Goynuk: Steam Activated/ZnCl ₂ -Catalyst		190	400
Goynuk: Steam Activated/ Acid Washed		210	370
Alpha: Pyrolysed	10		
Alpha: Steam Activated		170	280
Alpha: Steam Activated/ ZnCl ₂ -Catalyst		170	310
Alpha: Steam Activated/ Acid Washed		200	350

* 1 hour steam treatment using steam flow rates of 2 grams/minute

** 4 hour steam treatment using steam flow rates of 2 grams/minute

BET-surface area (calculated using standard BET equation [9])

Steam Activation at 880 C

Acid Washing with 0.5 molar HCl for 1 hour.



Figure 1 SEM micro-photograph showing PIP after steam pyrolysis of the Goynuk oil shale. The elongated cavities formed after volatilization of the alginite macerals. Char and mineral matter stabilize the macro-structure.



Figure 2 SEM micro-photograph showing SIP after steam activation of Goynuk shale char. Flaky surface with abundant macropores is depicted.

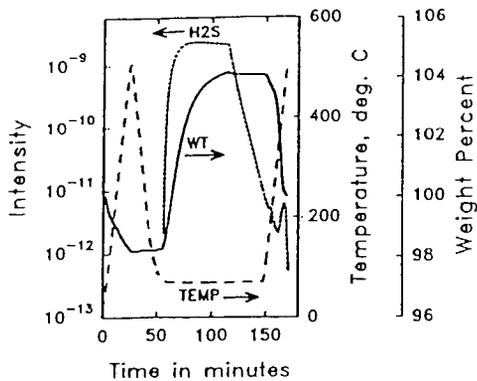


Figure 3 Temperature programmed adsorption/desorption analysis of the Goynuk adsorbent carbon. The carbon was activated at 880 °C using steam using ZnCl₂ catalyst. Mineral Matter was reduced after steam activation using 0.5 molar HCl.

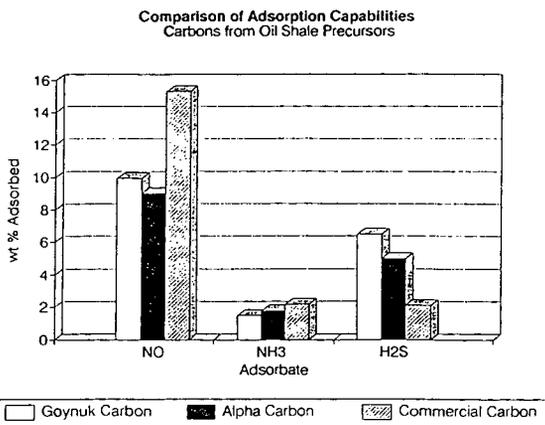


Figure 4 Comparison of the adsorption capabilities of Goynuk and Alpha derived adsorbent carbons with a commercial carbon. Goynuk and Alpha carbons have a BET surface area of about 350 m²/g. BET surface area of the commercial carbon corresponds to 450 m²/g.