Isothermal Pyrolysis and Combustion of Oil Shale in Steam

by

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ABSTRACT

In a solid-recycle retort, the burnt shale that serves as a heat carrier promotes coke formation. Steam inhibits coking reactions and has long been used for this purpose in hydrocarbon crackers. As part of a search for practical methods to minimize oil loss due to coking, we studied steam-moderated flash pyrolysis of Green River and Devonian oil shales. Volatile hydrocarbon production from a laboratory fluidized bed was monitored by using a high-temperature method that largely eliminated extraneous effects due to adsorption/desorption of oil vapors. Kinetics of oil shale flash pyrolysis in steam and in argon were comparable. The oil-plus-gas yield improved by 10±5% with wet (50% steam) rather than dry fluidizing gas; both raw and carbonate-free (acid-leached) shales were investigated. The fraction of carbon released by steam gasification of the char was shown to be insignificant.

The effect of steam on fluidized-bed experiments was compared with the effect on moving-bed, solid-recycle (pilot-scale) experiments and on temperature-programmed batch pyrolyses. Deuterium-exchange, carried out in the pilot retort, demonstrated the reactivity of hydrocarbon C–H bonds with high-temperature D2O. Deuterium oxide was more reactive than D2 at pyrolysis temperatures. Evidence for interaction of water vapor with hydrocarbon free radical intermediates was obtained; steam was shown not to react directly with kerogen or with the final pyrolysis products.

We also investigated the effect of steam on spent shale combustion. Inorganic-carbon-derived CO2 was detected when steam was present during combustion (just as during pyrolysis). Iron enriched carbonate-mineral surfaces explain much of the inorganic-carbon chemistry. The burnt shale disintegrated readily in steam/O2 and was much more prone to dust formation than when burned dry (i.e., in argon/O2).

INTRODUCTION

At the Lawrence Livermore National Laboratory, there is a continuing interest in steam retorting of oil shales. A considerable history of steam pyrolysis serves as the basis for this interest and for the work it has generated. Allred in his definitive patent and paper provides a review of prior work and gives persuasive arguments for steam as a beneficial additive to a Green River oil shale retort. Steam is claimed to improve yields of oil and H2, to allow lower pyrolyzer temperatures, and to produce a less caustic spent shale. However, a fluidized-bed steam retorting study of Devonian oil shale failed to fully confirm these claims.

We have recently measured isothermal kinetics of kerogen pyrolysis using a system that provides the temperature control needed for the study of high-temperature kinetics. Our data analysis gives a carbon balance, so nothing is missed and yield loss mechanisms can be identified. The system seemed particularly well suited for obtaining a better understanding of the steam pyrolysis of oil shale. We have also completed some laboratory and pilot-scale steam retorting studies that provide additional insight into the chemistry of kerogen pyrolysis.

With the techniques now available, we wanted to again ask the questions:
- Does steam increase the rate of kerogen pyrolysis?
- Can improved oil and H2 yields result from steam retorting, and does steam reduce coke formation?
- Does steam alter the chemistry of mineral matter reactions?
- What do steam/organic interactions say about oil formation/loss mechanisms?

We report here our preliminary results.
EXPERIMENTAL

Oil Shale Samples. Fluidized-bed pyrolyses were carried out on a 100-L/Mg (24-gal/ton) Green River Formation (Mahogany Zone) oil shale from the Anvil Points mine in Colorado (AP24), a 54-L/Mg (13-gal/ton) New Albany Shale of Devonian age from Kentucky (NA13), and a 105-L/Mg (25-gal/ton) Mahogany Zone oil shale from Tract C-a (CA25) that had been acid-leached for 24 hours in 6N H2SO4. Dust was removed from all these materials by cold fluidization. Table 1 provides elemental analyses and size information.

Table 1. Oil shales for fluidized-bed experiments: elemental analysis and sizes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Corg</th>
<th>%Carbonized</th>
<th>%Htot</th>
<th>Mesh Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP24</td>
<td>10.73</td>
<td>4.71</td>
<td>1.36</td>
<td>-40/+70</td>
</tr>
<tr>
<td>Leached CA25</td>
<td>12.53</td>
<td>0.03</td>
<td>2.32</td>
<td>-35/+60</td>
</tr>
<tr>
<td>NA13</td>
<td>11.80</td>
<td>0.44</td>
<td>1.42</td>
<td>-20/+35;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-35/+50</td>
</tr>
</tbody>
</table>

For temperature-programmed batch experiments, we used AP24 oil shale, -20/+70 mesh. Reagent-grade iron(II) sulfate (1 part to 10, -100 mesh) was added to the shale for one series of experiments. Pilot-scale, solid-recycle experiments used AP24 oil shale of size range 0.3 to 3.3 mm.

Bench-scale, Fluidized-bed Experiments. We dropped 200 to 500 mg of oil shale into a preheated fluidized bed of 100-g quartz sand sized from 180 to 300 μm (-50/+80 mesh). Usually, the bed also contained previously retorted and oxidized shale. Specimens were pyrolyzed isothermally at temperatures from 450 to 525 °C and at 4 to 10 psig. We first measured expelled volatiles, then burned away residual carbon on the spent shale at pyrolysis temperature to close a carbon balance. The bed was fluidized by 4 to 7 L/min (NTP) of a preheated argon/steam mixture (0 to 60% steam) containing 0.1% propane (pyrolysis) and then by argon/steam with propane and 20% v/v added O2 (char combustion). Propane produced a water and CO2 background even in the absence of steam. The bed was contained in a silica-glass tube (4.4 cm i.d.) held vertically in an electric furnace. There was a 3.5-psi pressure drop across the glass distributor plate and bed. The disengagement space above the bed had a volume of 0.76 L. Argon and products passed from the fluidized-bed pyrolyzer to the combustion tube through a line, 1 cm i.d. by 0.4 m long, which was heated by a tube furnace to bed temperature (±20 °C). At the combustion tube inlet, pyrolysis products mixed with preheated O2 (20% v/v) and burned over platinum gauze at 1000 °C.

Combustion products passed to an on-line Questor-1F (Extrel Corp.) mass spectrometer via a line held at 200 °C.

Bed temperature and concentrations of Ar, O2, CO2, and H2O were measured and recorded every 1 to 2 s. We calibrated for the noncondensable gases with commercially available analyzed gas standards and for H2O by burning propane in the combustion furnace to obtain a gas with a H2O:CO2 ratio of 1.333, which could be referenced to the CO2 standard.

Lag time and dispersion in the apparatus were determined by introducing n-octadecane coated on firebrick into the hot bed. Dispersion as a function of space velocity was used to correct the data, following a mathematical convolution procedure developed for this purpose. To collect pyrolysates from the fluidized bed, we replaced the combustion tube with two 500-cm3 traps packed with chole glass wool and held at 0 °C. Noncondensables exiting the traps passed via a pop-valve into evacuated gas-collection bottles (5000 cm3 volume). A three-way valve allowed two samples per experiment to be taken. Fluidizing gas was directed to waste until the shale (5 g, in this case) dropped into the 500 °C bed.

Other Retorting Experiments. Temperature-programmed pyrolyses were a modification of our standard method using steam (100%) rather than other gas sweeps. Pilot-scale, gravity-bed retort experiments have been described before.

Steam Generation. Steam generators were of conventional design, consisting of water pump, vaporizer section (tubing or capillary wound around a metal cylinder held at 300 °C in a tube furnace), ballast volume, valve or capillary to provide a back pressure of ~25 psig, argon inlet T, and three-way valve (so steam could be sent to the system or to waste, as desired). All lines were heat traced at >150 °C; a box oven at 200 °C held valves, ballast, and piping. We used a variety of water pumps sized for the flows required, including Milton-Roy Model DB-1-30R (fluidized bed) and DC-1-117R (pilot retort) hydraulic pumps with 1/8-in. pistons and Waters Assoc. Model 6000A HPLC pump (batch experiments).

Analytical Instrumentation. In-house methods available to us included the following: (1) elemental analysis by Heraeus CHN-O Rapid elemental analyzer, (2) temperature-programmed (2 °C/min) gas chromatography of oils by HP-5840 GC with FID using a 30-m DB-5 capillary column, (3) NMR of oils with a GE NT200 spectrometer running protons at 200 MHz and deuterium at 30.7 MHz, (4) solids by electron microprobe (JEOL Superprobe 733) using a Colorad mineral identification procedure, (5) dilute gas analysis with a magnetic sector VG-3001 MS (resolution 1 part in 2500), (6) hydrocarbon gas analysis by HP-5840 GC running a refinery gas analysis procedure.
RESULTS AND DISCUSSION

Kinetics. We expected our data from isothermal, fluidized-bed pyrolysis of Green River oil shale to show two types of carbon release, the first due to kerogen pyrolysis and the second to steam-promoted carbonate-mineral breakdown. In general, that was what we observed.

Figure 1 shows standard semilog plots of data from experiments with various proportions of steam in the fluidizing gas. The curves of Figure 1 superimpose for the first 80% of carbon release. Thus, volatile carbon-containing products are released from the kerogen at a rapid first-order rate (rate constant, \( k_1 \)) that is independent of steam content. The significant conclusion to be drawn from Figure 1 is that, contrary to what has been claimed,\(^6\) steam (up to 56 vol%) does not significantly increase the rate of kerogen pyrolysis.

We estimated rate parameters from our experiments and calculated \( T_{\text{max}} \) (where \( T_{\text{max}} \) is temperature at maximum carbon evolution for a 4 °C/min heating rate experiment); Table 2 compares our calculated result with what others have reported. We are in good agreement with Campbell,\(^4\) but do not see the rapid rate of pyrolysis in steam that Allred reported.\(^3\)

![Graph](image-url)

Figure 1. Pyrolysis of AP24 at 500 °C with various steam/Ar ratios. \( C/C_i \) is the fraction of volatile carbon released.

Table 2. Temperature of maximum hydrocarbon release from Green River oil shale at 4 °C/min heating rate.

<table>
<thead>
<tr>
<th>Sweep Gas</th>
<th>Temperature, °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Steam</td>
<td>400</td>
<td>Allred(^1)</td>
</tr>
<tr>
<td>CO₂</td>
<td>470</td>
<td>Allred(^1)</td>
</tr>
<tr>
<td>0 &amp; 56% H₂O/Ar</td>
<td>440</td>
<td>This work*</td>
</tr>
<tr>
<td>Autogenous</td>
<td>450</td>
<td>Campbell(^16)</td>
</tr>
</tbody>
</table>

* Calculated from isothermal kinetic data.

A second rate constant, \( k_2 \), due primarily to steam-promoted carbonate decomposition, can be estimated from the slopes of curves in Figure 1 at long times (as carbon release from kerogen pyrolysis decays to zero). As noted earlier, the carbonate-mineral decomposition rate depends on the steam content of the gas, and, as with most gas/solid reactions, the rate is not first order. At present, we hesitate to report rate parameters of this reaction for several reasons. (1) Carbon release continues at a low level for an extended time period; the correction chosen for background carbon release affects rate parameters greatly (this is true even when steam content = 0). (2) Our method counts as volatile carbon the carbon in very fine dust swept from the pyrolyzer through filters into the combuster; shale retorted in steam is especially soft and prone to dust formation. (3) System effects play a role; in particular, adsorption/desorption of oil on surfaces can be important in a dusty system.\(^11\) (4) Slow methane release and steam gasification of char may further complicate matters. Problems with determining \( k_2 \) compromise efforts to specify \( k_1 \) accurately.

We flush pyrolyzed carbonate-free oil shale, dry and in steam, in an attempt to circumvent problems associated with inorganic-carbon release. However, carbonate-free oil shale was even drier than when steam retorted and up to 50% of a presumably more acidic dust blew from the bed. System effects (primarily adsorption/desorption of vapors) similar to those encountered with Devonian oil shale were noted.\(^11\) We will delay reporting new \( k_1 \) and \( k_2 \) values until we can improve on what is presently in the literature.\(^9,^{10,16}\)

Reaction of Steam with Minerals. Burnham et al. have summarized what we know of carbonate-mineral reactions in steam.\(^4\) Steam-promoted dolomite decomposition is a source of some carbon released by flash pyrolysis. For ankerite, this reaction can be written as:

\[
3\text{CaMg}_\text{Fe}(\text{CO}_\text{3})\text{H}_\text{2}O + (1-x)\text{H}_\text{2}O \rightarrow 3\text{CaCO}_\text{3} + 3\text{MgO} + (1-x)\text{Fe}_\text{2}O_\text{3} + (1-x)\text{H}_\text{2} + 3\text{CO}_\text{2}. \tag{1}
\]

This reaction (actually a set of reactions) is slow and of marginal importance in the absence of steam. It accelerates as a function of steam partial pressure. At high temperature, steam is known to catalyze formation of calcium-containing silicates.\(^1\)

Only rarely does a pyrolysis reaction rate depend on the gaseous environment. As such, steam-promoted carbonate decomposition might best be viewed as acid-catalyzed carbonate decomposition. Available protons convert carbonate salts to unstable bicarbonates (e.g., sodium carbonate melts at 850 °C; the bicarbonate decomposes at 270 °C). Adsorbed water vapor is an excellent solvent for protons, and water (via self-ionization) is a good acid at 500 °C. Acids other than water, such as H₂S and phenols, may contribute but probably are minor proton sources, given the high water content of the
sweep gas. Since steam alone has been reported to catalyze the decomposition of sulfur-free dolomite, acids in addition to water are apparently unnecessary.3,7

Associated metal ions will have only a secondary role in the acid-catalyzed conversion of carbonates to oxides. However, the instability of FeO relative to Fe₂O₃ at these temperatures makes iron a special case. In addition, the chemistry of iron in the oil shale's carbonate minerals changes with steam present. Reactions with and without steam present are as follows, although iron will be primarily as ankerite (decomposition temperature >500 °C), see reaction (1), rather than siderite, FeCO₃ (decomposition temperature ≈500 °C):

Dry: \( \text{FeCO}_3 + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{CO}_2 + \text{H}_2\text{O} \)  \( (2) \)

Steam: \( 3\text{FeCO}_3 + \text{H}_2\text{O} \rightarrow 3\text{FeO} + 3\text{CO}_2 + \text{H}_2 \)  \( (3) \)

The \( \text{H}_2 \) and its precursors generated by reactions (1) and (3) serve as a source of hydrogen needed to improve the hydrocarbon product yield. We show magnetite, \( \text{Fe}_3\text{O}_4 \), as another product of these reactions because we believe that reactive carbon and hydrogen donors set the oxygen fugacity at about this level. However, most iron remains unreacted during pyrolysis and any magnetite converts to hematite, \( \text{Fe}_2\text{O}_3 \), during combustion. Less group II metal oxides, in part, account for steam producing a less caustic spent shale.6,7

Gas/solid reactions, such as the steam reaction with carbonate minerals, occur at solid surfaces. We focus on iron chemistry because of a recent observation that iron is concentrated here. Figure 2 is a digitized microprobe photograph of carbonate-mineral grains in a sample of Green River formation oil shale. The method for obtaining such photographs was developed by Don McCoy at our Laboratory specifically for the study of nonstoichiometric materials and was a 1986 IR-100 award winner. It has been valuable for visualizing oil shale mineralogy.18 The original color photograph is more informative, but zoned carbonate minerals can be identified in the oil shale of Figure 2.

Zoning of native carbonates is well known. Katz19 treats a specific example and cites a dozen reports that precede his 1971 paper. In Green River oil shale, we observe carbonate-mineral assemblages of three principal types: [A] pure calcite (greater than 90% calcium cations), [B] impure dolomite, [C] zoned carbonate-mineral mixtures. Calcite (type [A]) is often the least significant of the three types. Dolomite (type [B]), with its distinctive rhombohedral crystal form, is easily recognized. Iron freely substitutes for magnesium throughout the interior of these crystals, but iron content is primarily in the usual dolomite/ankerite range (less than 10% of the total Ca²⁺/Mg²⁺/Fe³⁺, appears light relative to the grey shades of Figure 2). Toward grain boundaries, dolomite of crystal type [B] becomes increasingly iron rich with high-iron-content ankerite eventually giving way to a magnesium/iron solid solution that is nearly calcium free (dark). Iron is often the predominant metal ion right at a surface (thin light dots) and is sometimes the only one of the metal ions identified there. Such zoning near edges occurs when iron from a relatively high-iron-content solution substitutes into dolomite crystals in a stagnant, reducing environment.18

Mixtures (type [C]) often predominate. They have a calcite core (light) and an unremarkable crystal form. Moving away from the core, there is a step change to dolomite (light). Magnesium incorporation into the calcite (dark) precedes this step change (the phase diagram only allows solid solutions with greater than 90% and with 50% calcium). Progression toward an iron-rich surface occurs, just as with minerals of type [B]. Our resolution (0.5 µm) does not permit an unambiguous distinction between mixtures and solid solutions, but we have attempted to make the above explanation consistent with published phase diagrams.18,20 As a result of such zoning, iron participates in surface reactions to a greater extent than one would predict from the bulk iron content.

Gas Production. Product gas distribution provides clues for understanding how steam alters the chemistry in a retort. Minerals account for most of the CO₂ produced during steam retorting [see reactions (1) and (3)]. A higher H₂S-content pyrolysis gas from steam retorting is due, in part, to reaction (2) becoming unfavorable as water content of the gaseous environment increases. In fact, hydrolysis of iron sulfides (pyrrhotite, for example) generates H₂S:

\( 3\text{FeS} + 4\text{H}_2\text{O} \rightarrow 3\text{FeO} + 3\text{H}_2\text{S} + \text{H}_2 \)  \( (4) \)

This reaction—as well as reactions (1) and (3)—serves as a source of H₂, a particularly important gaseous product.

Table 3 gives typical product-gas compositions from dry and steam retorting under temperature-programmed batch pyrolysis conditions (4°C, 200 cm³/min sweep). Acid gases, CO₂ and H₂S, were removed (40% CO₂ removed in the steam
case, 13% in the dry). Throughout, we express flow rates as volume at NTP, as though water were gaseous (flow, of course, increases with increasing temperature for experiments such as those of Table 3).

Similarities in Table 3 are more striking than differences. The slightly higher ratios of propylene:propane and ethylene:ethane from steam correlate with a slightly higher oil yield (see below). For experiments such as this where coking is the major oil loss mechanism, alkene:alkane ratios are good predictors of oil yield. In steam, there is a balance with less H₂ from coking but more from reactions (1) and (4). Hydrogen gas is only one co-product that accompanies magnetite formation. The precursors to H₂ are reactive intermediates that contribute to the pool of hydrogen donors on particle surfaces. These intermediates can, of course, release H₂, but they can also convert pyrite or other sulfur species to H₂S, cap free radicals to form hydrocarbons, and reduce carbonates, or perhaps CO₂ to CO and water.

Table 4 compares gas yields from laboratory fluidized-bed pyrolysis of the AP24 shale in steam and in argon. To facilitate comparison, we express gas formation as mMole/g of raw shale and include acid gases. More H₂S and CO₂ from steam retorting is consistent with the chemistry outlined above. Hydrogen comes primarily from coking and cracking of hydrocarbon intermediates, particularly toward the end of oil generation. Thus, at longer times, the dry-gas sweep experiment yields more H₂ (and coke) than does steam pyrolysis.

The gas ratio, [CO]/([H₂]/[CO₂]), is similar with or without added steam (see Table 4). Thus, gas-phase equilibration via the water-gas shift reaction does not occur at this temperature. However, hydrogen donors more reactive than the H₂ required by the water-gas reaction can also convert inorganic carbonates (or CO₂) to CO. This hydrogen-donor variation of the water-gas reaction is of interest since the H₂O concentration at active surface sites differs from the gas-phase concentration. We are investigating this reaction, but we conclude from Table 4 that under dry conditions CO accounts for less than 0.6% of the total carbon evolved and steam (60% in argon) releases less than 0.2% more carbon as CO₂.

Gasification of char by steam at 500 °C is not anticipated, but the freshly deposited carbon burns readily even at 450 °C and may be unusually reactive. Figure 3 shows the results of a steam gasification test using our fluidized-bed pyrolyzer and the AP24 oil shale. An upset attributable to the change in gas flow pattern is noted as char combustion commences. The introduction of steam caused an upset, too, so our estimate of the small amount of carbon released by steam gasification has some uncertainty (i.e., ±1%). This release agrees well with the expected additional CO₂ from steam-promoted carbonate decomposition [reactions (1) and (3)] based on CO₂ production with steam (pyrolysis/gasification) and without (pyrolysis only) as given in Table 4. Of course, we cannot exclude the possibility that as charring progresses the carbon residue at some stage is more susceptible to gasification, although the low CO content of the gas (see Table 4) implies that in no case is steam gasification really important.

**Shale Oil Yield.** How steam affects oil yield is a key issue. We looked carefully at both isothermal and temperature-programmed retorting experiments in the laboratory and the pilot plant in an attempt to pinpoint important factors. Table 5 shows results from a series of temperature-programmed batch retorting experiments. We include in Table 5 results from experiments with iron(II) sulfate present. This additive is known to promote coking.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sample</th>
<th>Steam*</th>
<th>Dry*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1st min</td>
<td>0.228</td>
<td>0.128</td>
</tr>
<tr>
<td></td>
<td>min 1-2.5</td>
<td>0.057</td>
<td>0.013</td>
</tr>
<tr>
<td>CO</td>
<td>1st min</td>
<td>0.048</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>min 1-2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>1st min</td>
<td>0.080</td>
<td>0.133</td>
</tr>
<tr>
<td></td>
<td>min 1-2.5</td>
<td>0.035</td>
<td>0.059</td>
</tr>
<tr>
<td>CH₄</td>
<td>1st min</td>
<td>0.0065</td>
<td>0.073</td>
</tr>
<tr>
<td></td>
<td>min 1-2.5</td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>H₂S</td>
<td>1st min</td>
<td>&gt;0.003</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td></td>
<td>min 1-2.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* mMole gas/g raw shale; the bed was 100 g of clean sand for the steam experiment, 100 g of sand and 10 g of burnt oil shale for the dry experiment.

Table 3. Gas composition from 4 °C/min batch pyrolysis of AP24 oil shale [200 cm³/min sweep (NTP)].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole %</th>
<th>Steam</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>5.0</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>45.3</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>23.6</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>C₂H₄</td>
<td>2.2</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>7.9</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>3.2</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>C₇H₄</td>
<td>4.0</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>C₄'s</td>
<td>5.1</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>C₅'s</td>
<td>2.4</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>C₆+</td>
<td>1.3</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

* Stripped of acid gases. Under dry conditions in argon, 13% CO₂ formed; with steam sweep, 40%.
steam. Additive baths have repeated. Karl-Fischer on nearly section, Table 3. Pyrolysis of shale. AP24 + 10% FeSO4·7H2O Argon, 60 cm³/min 20.4 Argon, 100 cm³/min 22.1 Steam, 200 cm³/min 23.6 * Sweep rates given in terms of gas volume at 25°C.

Truly comparable argon and steam experiments are nearly unattainable. Obstacles include incomplete condensation, aerosols, oil/water separation problems, and non-uniform low steam flows. Other investigators have previously commented on these difficulties and their detrimental effect on repeatability. However, we have applied some fixes: (1) ice/salt baths for condensation, (2) extended separation time, (3) Karl-Fischer analysis of the total product, (4) monitoring of the steam flow rate by mass spectroscopy. Table 5 gives the results of our best efforts.

We confirm the significant impact of sweep-gas flow rate on oil yield. At high sweep rates (argon or steam), the coke-producing additive FeSO4·7H2O was nearly ineffective. When steam replaced argon (flow rate and condensation/separation efficiency being equal), a small (less than 5%) but real increase in oil yield was realized. This yield enhancement is small enough to go unnoticed at most practical heating rates and flow rates. Rubel and Davis investigated Devonian oil shale pyrolysis at various steam pressures and flows. They documented the beneficial effect of rapid sweep but found no evidence for oil yield enhancement directly attributable to steam. Steam retorts have often used a gas (steam) as heat carrier. To achieve good throughput and near isothermal conditions, a rapid steam flow rate is desirable. Allred, for example, used a minimum space velocity that was comparable to our fluidization velocity; his maximum space velocity was five times our maximum.

The strong particle-size dependence of oil yield from steam retorting that Campbell and Taylor reported has been largely ignored by investigators. Our failure to see any significant yield improvements when we introduced steam at low sweep rates into our gravity-bed pilot retort (isothermal, solid-recycle conditions) can be attributed to the shale size (0.3-3.3 mm) used for these experiments. In one pilot retort experiment, for example, steam rather than nitrogen was passed through the retort head-space in an attempt to deactivate the heat carrier. Slightly more H2S and CO2 were produced, but oil yield and spent shale residual carbon were the same to within our usual uncertainties (about ±3%).

Oil plus-gas yield from the fluidized-bed retort. The laboratory fluidized bed with combustion tube that we used for kinetics experiments offered a sensitive method for quantitatively measuring hydrocarbon yields in the presence of burnt shale. It provided convincing evidence for improved yields in steam. Comparable, rapid sweeps were easily maintained; formation of CO in the fluidized bed and by Fischer assay matched, so there was no error in yield from this source. Carbonate-mineral decomposition with release of CO2 did complicate the yield determination when steam was sweep gas, but we eliminated this problem by using oil shale that had been acid leached to remove carbonates. Alternatively, we measured the inorganic carbon released by AP24 oil shale and used the rate expression to estimate and subtract away the proportion evolved during the pyrolysis and combustion stages. Figure 4 shows the improved oil plus-gas yields from steam retorting carbonate-free (H+ leached) oil shale in the fluidized bed. Material used for the steam experiments contained less than 0.05% inorganic carbon, as determined by acid-evolved CO2. Organic-carbon balances for these steam experiments were excellent. The average carbon content of six carbonate-free shale samples dropped sequentially into the bed (as determined by the on-line mass spectrometer) was 12.7 ± 0.2%. The carbon content was 12.56 ± 0.19% by elemental analysis (see Table 1).

The x-axis of Figure 4 is related to "recycle ratio", provided no spent shale has been lost from the bed. Dust is an important complication. Its formation depends on several variables including temperature, time, sweep rate, shale grade and size, and steam content of the gas. We measured, semi-quantitatively, the dust produced when a 24-gal/ton Colorado
oil shale which had been carefully de-dusted by cold fluidization was heated in our retort for four hours (dry: 5-10% dust; 1:5 steam/Ar: 15% dust; carbonate-free in 1:1 steam/argon: 40-50% dust). The two data points shown as open diamonds on Figure 4 were from carbonate-free shale in argon and came after the series of steam experiments. These points are displaced to the right along the x-axis to an extent related to the fraction of shale lost from the bed. A rough correction for lost dust would place the points right on the usual line.

For fluidized-bed experiments such as these, steam increased the hydrocarbon yield by 10 ± 5%. Coking losses on burnt shale in the bed were reduced, and at all recycle ratios, yields in steam were above Fischer assay. Results were the same when carbonate-containing Green River oil shale was flash pyrolyzed in steam; we obtained high yields from small particle-size AP24 over a wide range of conditions. Thus, from 13 experiments with burnt/raw ratios ranging from 0 to 4, temperature ranging from 475 to 525 °C, sweep-gas steam content ranging from 16 to 56%, and fluidization velocity ranging from 3.5 to 6.5 L/min (NTP), 86.5 ± 2% carbon evolved as oil-plus-gas-plus-dust (we estimate the maximum dust contribution at less than 2% and usually less than 1%). This can be compared with the shale’s oil-plus-gas yield of 76.9% organic carbon, by Fischer assay.

Figure 5 shows results of a similar set of experiments with Devonian oil shale (NA13 containing less than 0.5% inorganic carbon, see Table 1). To reduce dust, a slightly larger size of shale (~20/+35 mesh) was used. As with the Colorado oil shale, steam gave an increase in volatile carbon release. A similar yield improvement with 3% ammonia in argon as fluidizing gas (see Figure 5) suggests that ammonia is similar to water vapor as a coking inhibitor. Active sites where coke formation occurs may well be acidic.

Steam and the Mechanism of Shale Oil Formation.
We understand kerogen pyrolysis and oil formation in terms of a free radical mechanism that is characterized by a rather large population of free radical intermediates. Precursors of the linear hydrocarbons produced from kerogen participate in a free radical steady state similar to that achieved when, for example, n-butane is pyrolyzed. This steady state condition, if established, results in the gases methane, ethane, ethylene, and propylene being produced in a characteristic molar ratio, β, where

\[ \beta = \frac{[\text{C}_n\text{H}_{2n+2}] + [\text{C}_n\text{H}_{2n}] + [\text{C}_n\text{H}_{2n-2}]}{[\text{C}_2\text{H}_6] + [\text{C}_3\text{H}_8]} \]

and β from fluidized-bed kerogen pyrolysis has the same value as that from cracking of n-butane. The ratio β from retorting in argon is 0.50; from retorting in steam, 0.51. These are identical numbers to within our precision—the very dilute mixtures were analyzed by mass spectroscopy.

Identical β values with and without steam suggest that steam does not alter the nature of this free radical steady state and, thus, plays no part in determining the relative concentrations of these important intermediates. Furthermore, the rate determining step for kerogen pyrolysis must have a transition state with which water in no way interacts since, as noted earlier, steam has no effect on the pyrolysis kinetics. Yield improvements realized when small particles are retorted in...
steam must come from a steam-induced shift in the importance of parallel reactions which convert intermediates to oil or to char. Steam must either help in the conversion of free radicals to oil or interfere with the char forming process. Oil components, once formed, coke very little under these conditions, and steam does not inhibit such coking.27

To test for the interaction of steam with intermediates present during retorting, we introduced a slow sweep of D2O into the pilot retort (gravity bed, 4:1 solid-recycle ratio, isothermal at 475 °C). The oil was analyzed for incorporation of the isotopic label with 2H-NMR (D-NMR). Figure 6 shows a usual 1H-NMR spectrum of oil obtained from this retort under normal circumstances (N2 sweep); Figure 7 shows the D-NMR spectra of oils obtained with D2O sweep, with D3 sweep, and with H2 sweep.

The D-NMR spectra are of neat shale oils and have similar sensitivities with regard to deuterium content. With spectral data displayed in this way, naturally occurring deuterium was invisible (see Figure 7, H2 sweep). Oil generated with D3 sweep had only a small amount of deuterium incorporation; less than 0.3% of the oil protons exchanged (see Figure 7, D3 sweep). With D2O sweep, there was substantial exchange; the fraction of deuterium in oil hydrocarbons (5.3%) was more than 70% of the H:D ratio for all materials fed into the retort (see Figure 7, D2O sweep). The more stable free radical sites (allylic, benzylic, and α to heteroatoms) exchanged more completely, but all hydrocarbon protons exchanged to a considerable extent (even strongly bound vinyl and aromatic protons).

Steam, of course, contributes in a small way to the hydrogen donor pool as it converts iron compounds to mag-

![Figure 6. Proton NMR spectrum of shale oil from the pilot retort (N2 sweep).](image)

![Figure 7. D-NMR spectra of shale oils produced with various sweep gases (extracted with H2O to remove dissolved D2O).](image)

**CONCLUSIONS**

In a retort, the influence of steam on chemistry is limited to surface reactions. Steam slows coke formation that occurs on active surface sites; its impact is most noticeable when the shale's average particle size is small (more surface area). In the presence of steam, we obtained a 10 ± 5% increase in hydrocarbon release from a laboratory fluidized-bed pyrolyzer at all solid-recycle ratios. However, steam had no influence on the rate of kerogen pyrolysis and did not significantly alter the ratio of important free radical intermediates in the gas phase. No steam gasification of carbonaceous residue could be detected with the methods available to us,
and char/steam reactions may well be insignificant at typical pyrolysis temperatures (500°C and lower).

Steam does accelerate dust formation. Both Green River and Devonian oil shale when pyrolyzed and burned in steam become much softer and disintegrate more readily than when pyrolyzed and burned in argon. Since the Devonian shale also deteriorates, such softening cannot be due totally to carbonate-mineral decomposition and silicate formation; iron sulfide oxidation/hydrolysis may also contribute. After combustion in steam, Devonian oil shale (original carbon content 12.2%, <0.5% inorganic carbon) became so soft that it could be rubbed between the fingers to a brown smear. A soft spent shale was the result of burning in steam, regardless of the pyrolysis procedure. Certain retorting options can take advantage of this observation. In particular, methods that use an inert solid heat carrier might benefit from a separation procedure that converts spent shale to fines. Such methods should be especially well suited for the rich oil shales that will be of initial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge R. L. Braun for help in treating kinetic data. Temperature-programmed batch pyrolyses using steam were carried out by K. Foster; R. Swansiger obtained the elemental analyses and made the acid-evolved CO₂ measurements; J. Happe supplied proton and deuterium NMR spectra. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-Eng-48.

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