

Isothermal Pyrolysis and Char Combustion of Oil Shales

by

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ABSTRACT

Yields and rates of hydrocarbons evolved during pyrolysis of oil shales have been measured with improved accuracy. Green River and New Albany oil shales were heated in a fluidized sand bed, and volatile pyrolysis products were transferred to a combustion tube and burned. Resulting H_2O and CO_2 were detected in real time by mass spectrometry. Residual char was subsequently burned to allow complete C and H balances. Good closure was obtained. Proportions of organic C and H released as pyrolysis products and retained as char were determined. Shale oil loss due to the presence of oxidized shale in the fluidized bed was measured accurately.

We find that all of the experimental apparatus that the pyrolysis gas contacts must be near pyrolysis temperature to avoid condensation of heavy oil which subsequently forms coke and secondary products. We observe a faster release of products with all transfer lines at $450^\circ C$ than when they are at $300^\circ C$. The current uncertainty in pyrolysis rates is due in part to such difficulties with experimental technique.

INTRODUCTION

One of the most important oil shale processing parameters is the rate of hydrocarbon product formation. However, considerable disagreement exists concerning the time required to release hydrocarbons from an oil shale.[1-5] Estimates from studies that use different experimental techniques often vary greatly. In general, isothermal experiments predict longer pyrolysis times and more complex patterns of hydrocarbon release than do non-isothermal experiments. Even for a single technique such as fluidized-bed pyrolysis, we believe that the time required for 98% hydrocarbon evolution from Green River oil shale is uncertain by at least a factor of 5. For example, 0.9 min at $500^\circ C$ was reported in 1956[1], although recently we, and also researchers at Chevron Research, concluded that about 6 min were needed.[2-4] At the Lawrence Livermore National Laboratory (LLNL), because we are investigating solid-recycle retorting, which is an isothermal process, we would like to resolve these differences.

Some components of a flash-pyrolysis oil have high molecular weights or are unstable, making condensation and coke formation in transfer lines a possible source of experimental problems. Recent determinations of pyrolysis kinetics have measured hydrocarbon concentrations with a flame-ionization detector (FID) operating at $300-350^\circ C$. [2,4-6] Also, heating any apparatus uniformly to near $500^\circ C$ is difficult, particularly glass tubing used for gas-transfer lines. Laboratory heating tapes typically have an upper temperature limit of about $450^\circ C$; furthermore, experimentalists rarely use good temperature controllers with heating tapes. We report here the results of experiments that kept oil condensation and secondary reactions to a minimum by keeping transfer

lines hot and by using a combustion device and mass spectrometer (MS) in place of the FID to monitor hydrocarbon evolution.

EXPERIMENTAL

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, USA (AP24), and on a 54-L/Mg (13-gal/ton) New Albany Shale of Devonian age from Kentucky, USA (NA13). For one set of pyrolysis experiments, we used AP24 treated with HCl to remove mineral C. The AP24 shale contained 10.5% organic C and 1.47% total H; the NA13 shale contained 12.0% organic C and 1.42% total H. Both shales were ground to a size range of 300–425 μm , and dust was removed by cold fluidization.

We dropped 550 mg of ground oil shale into a preheated fluidized bed (see Figure 1) containing 100 g of quartz sand 180 to 300 μm in size. For most experiments, the bed also contained some previously retorted and oxidized shale. The bed was fluidized by 4 L/min (STP) of Ar (pyrolysis) and then by Ar containing 20% v/v O_2 (char combustion). Preheated fluidizing gas was introduced through a glass distributor plate into the bed contained in a silica-glass tube (4.4 cm i.d.) positioned vertically in an electric furnace. The disengagement space above the bed had a volume of 0.76 L. The Ar and product gases were transported from the fluidized-bed pyrolyzer to a combustion furnace through a tube, 1 cm i.d. by 0.4 m long, which was heated by glass-insulated tapes (usually to 450°C). At the entrance to the combustion furnace, the product stream was mixed with 20% v/v O_2 and burned over platinum foil at an 800°C furnace temperature. Combustion products passed to an on-line mass spectrometer through a line heated to 150°C. Concentrations of Ar, O_2 , CO_2 , H_2O , CO, CH_4 , and SO_2 were measured and recorded every 2 s. The mass spectrometer was calibrated for the non-condensable gases using commercially available analyzed gas standards. We calibrated for H_2O by burning propane in the combustion furnace to obtain a gas with a H_2O -to- CO_2 ratio of 1.333, which could be referenced to the CO_2 standard.

We carried out investigations at temperatures from 450 to 525°C, but primarily at 475°C. Dispersion in our apparatus was measured by introducing octadecane coated on firebrick into the hot bed or by injecting a slug of gaseous CO_2 . At 475°C, the highest temperature for which accurate rate data could be obtained without a dispersion correction, both methods gave a CO_2 peak with a half-width of 5 s; the concentration of CO_2 fell to 1/10 of the maximum value in 14 s. The rate of sample heating could be ignored at 475°C because the time required for cold raw shale to come to within 1°C of the bed temperature was calculated to be 3 s.

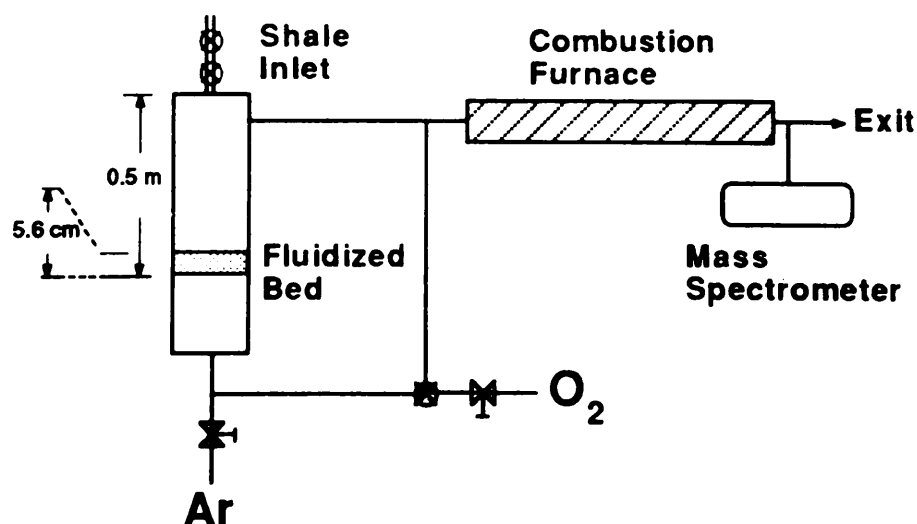


Figure 1. Schematic of our apparatus for fluidized-bed pyrolysis and char combustion. The detector, a combustion tube followed by a mass spectrometer, gives the rate of C and H release on an elemental basis by measuring CO_2 and H_2O concentrations.

RESULTS

Concentration-time profiles of CO_2 and H_2O were obtained during both retorting (when effluent hydrocarbons were burned outside the fluidized bed) and during combustion of the char in the retorted shale (which took place when O_2 was directed into the fluidized bed to burn residual organic C). Figure 2 shows our experimental results for pyrolysis and subsequent combustion of AP24 and NA13 oil shales at 475°C . Integration of these profiles gave the amount of C and H released by retorting and then by combustion of the retorted shale. The C and H mass balances closed to within 10%.

Table 1 shows our pyrolysis products' H/C ratios and a similar ratio calculated from the raw shale elemental analysis. An $\text{H}/\text{C}_{\text{org}}$ is given for the raw shale, with H data corrected for high-

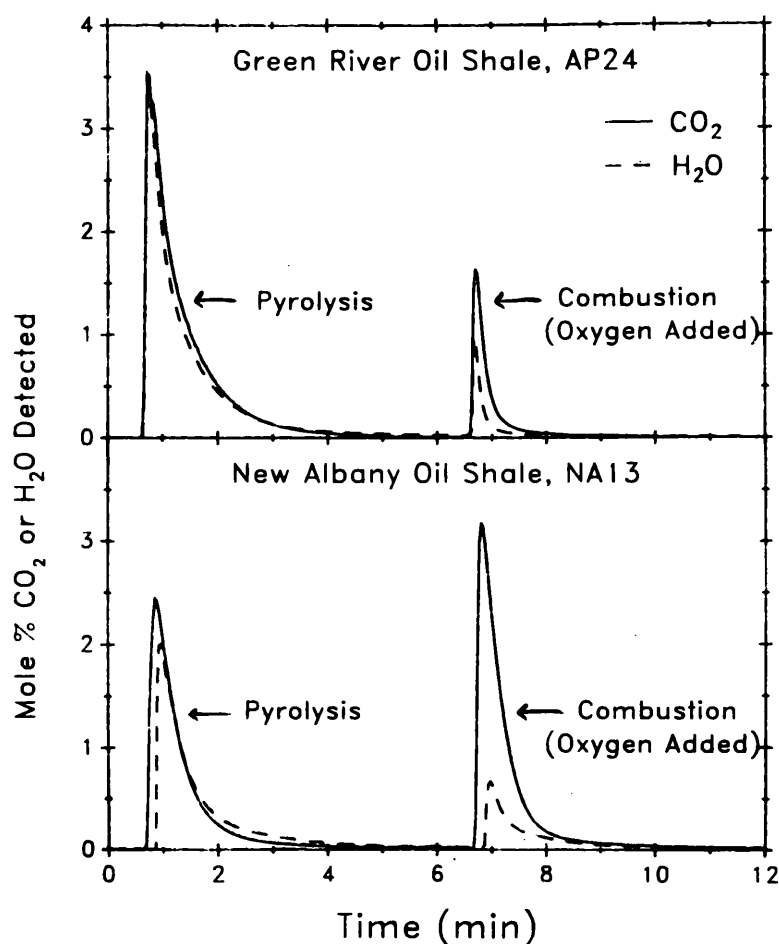


Figure 2. Raw experimental data for fluidized-bed pyrolysis and char combustion at 475°C . Volatile pyrolysis products passed through a combustion tube before detection. The amount of CO_2 in the gas streams after pyrolysis and char combustion matches the organic C content of the shales.

Table 1. H/C ratios for fluidized-bed pyrolysis.

The Experiment		H/C Elemental Ratios			
Shale	Bed Temp. ($^\circ\text{C}$)	Raw Shale*	Volatile Products	Char	Total Products
AP24	450	1.6	2.2	0.8	1.7
	475		1.8	0.8	1.6
	500		1.8	0.5	1.6
	525		2.0	0.4	1.6
NA13	475	1.2	1.8	0.5	1.1

*Corrected (see text).

temperature mineral water using assay data and estimates of mineral matter composition. For AP24, results were 1.47% total H and 0.15% mineral H (most from analcime), so <0.05% high-temperature mineral H.[7,8] For NA13, results were 1.42% total H and 0.4 mineral H, most from clays that release about half their water when heated to 475°C.[7-9] Our results confirm a very low H/C ratio for the kerogen of Devonian Shale.[9] The H/C ratio of char—which has an important influence on its combustion properties—decreased as the pyrolysis temperature increased. Volatile flash-pyrolysis products had a lower H/C ratio than Fischer assay oil/gas/water. However, recovery of volatiles from AP24 flash pyrolyzed at 475°C was 8% more than Fischer assay; for NA13, the increase over assay was 32%.

Pyrolysis rates were calculated from slopes of curves showing the log of the fraction of pyrolysis C remaining as a function of time (see Figure 3). Rates were also obtained by means of an LLNL chemical kinetics analysis computer program.[10] Pyrolysis rates for AP24 can be formulated by a single first-order rate constant, whereas two rate constants are required for a good fit of the NA13 data. The final 10% of the hydrocarbons are released from NA13 at a lower rate, but the overall pyrolysis rate for NA13 is a little faster than for AP24. Figure 4 shows our experimental data and calculated fits.

Our C-release data for AP24 pyrolysis at 475°C was consistent with a simple first-order reaction mechanism, as judged by reduced-time plots, which provide a sensitive test of reaction type.[5] This was not so for 450°C data. Carbon evolved from acid-treated AP24 shale at the same rate as from shale that had not been acid leached, indicating that CO₂ evolution from carbonate minerals is insignificant relative to hydrocarbon evolution at 475°C. For AP24, rates calculated from H evolution agreed well with those from C evolution. For NA13, after evolution of organics has decayed to near zero, continued mineral water release at 475°C (see Figure 2) prevents a satisfactory kinetic analysis based on H data. At 450°C, relative rates of C and H release from NA13 match somewhat better.

Figure 5 shows the effect of transfer-line temperature on the apparent rate of AP24 pyrolysis. In this example, the fluidized-bed temperature was 475°C, while temperature of the transfer line was 300°C in one case and 450°C in the other. For the first 12 s, during which time pyrolysis is about

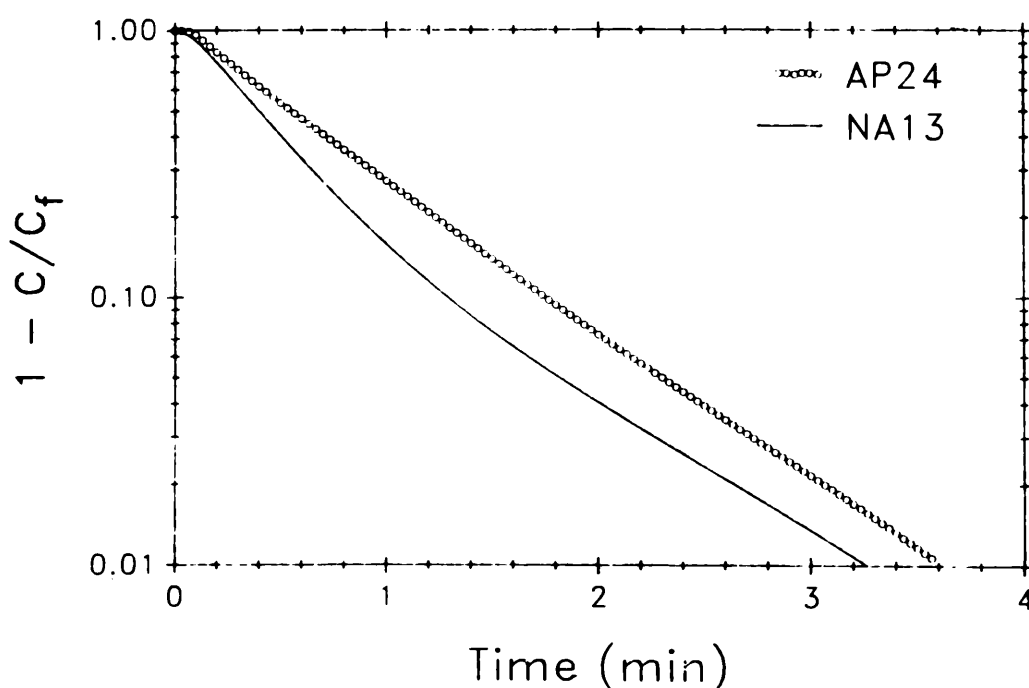


Figure 3. AP24 shale pyrolysis at 475°C gives the linear semilog plot expected of simple first-order kinetics; NA13 shale does not. The final amount of C released by pyrolysis is designated C_f. 1-C/C_f is the fraction of pyrolysis C remaining.

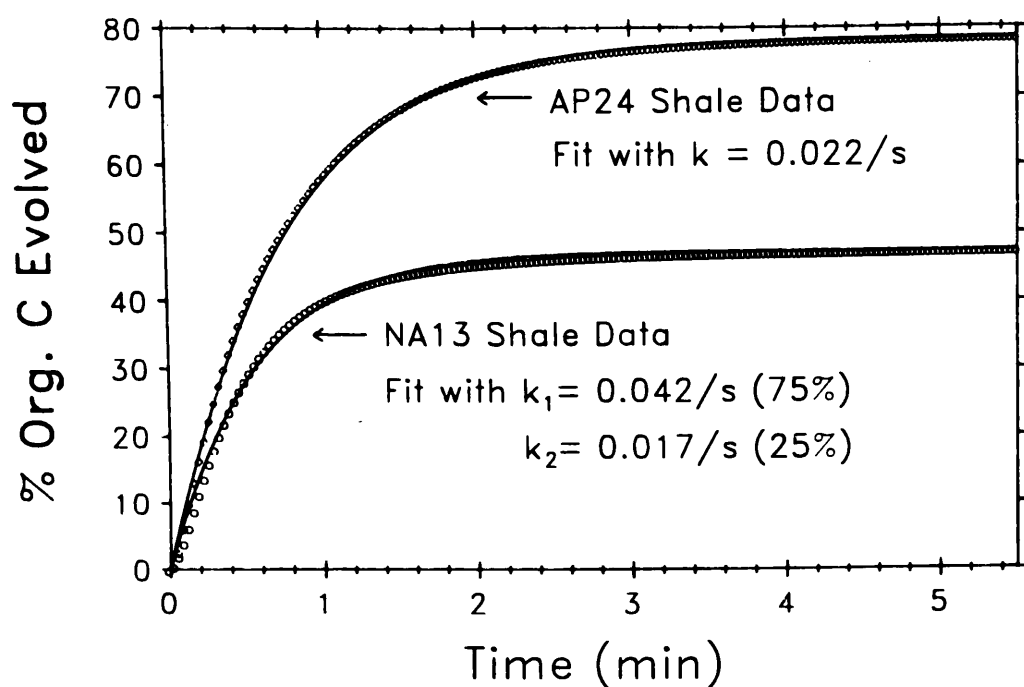


Figure 4. Same experiment as Figure 3, 475°C with a burned/raw shale ratio = 2, showing pyrolysis data expressed as the percent of total organic C in the raw shale. The fit to data by our rate constants is also shown. The % reacted by each rate expression is given when data required a fit by parallel reactions (NA13).

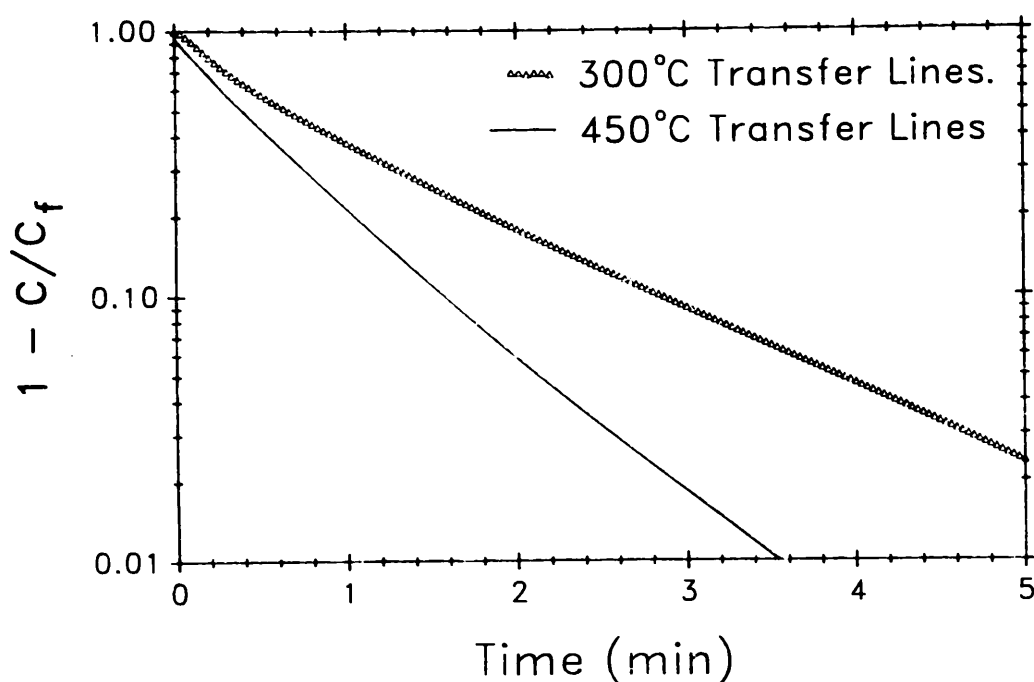


Figure 5. Oil vapors from flash pyrolysis of AP24 shale at 475°C can condense and coke if the transfer-line temperature is too low. In such cases, artificially low pyrolysis rates, requiring more than one rate constant, are obtained.

40% completed, the rate constant appears to be nearly independent of transfer-line temperature, but thereafter the cooler line suggests a rate constant that is smaller by a factor of 2. Less oil vapor reached the detector when the line was cool, and subsequent char combustion released more of the total carbon because it also burned C in the line. We suspect that the heaviest oil fraction condenses in the 300°C line when the oil evolution rate is fast and effluent partial pressure is high. The oil polymerizes to coke, or it revaporizes when oil partial pressure is sufficiently low, giving rise to a long tail on the C-release curve.

In many cases, burned oil shale from previous experiments was present in the fluidized sand bed. The fraction of raw shale organic C recovered by pyrolysis decreased as the amount of burned shale increased. There was a corresponding increase in the amount of char formed. This is of special interest because shale retorting by means of direct contact with hot recycled shale appears to have commercial potential as a means to achieve high heating rates. Figure 6 shows the progressive decrease in the fraction of organic C volatilized as a function of the ratio of oxidized shale to raw shale in the bed (this corresponds to a recycle ratio). Also shown is the recovery of C as oil and gas by Fischer assay. With no oxidized shale present, 108% of the Fischer assay yield is recovered from the AP24 shale by flash pyrolysis; the yield drops to 97% when the burned/raw ratio is 4. DiRicco and Barrick obtained an oil-plus-gas yield of 95% Fischer assay by flash pyrolyzing an AP shale at 465°C with a burned/raw ratio of 5.6[1]; from our work, we would predict

94% of assay. Oil loss due to burned shale was even more dramatic in the case of NA13 shale (see Figure 6). We also noted a decrease in the product yield when pyrolyzed shale (not oxidized) was present in the bed.

In our experiments, combustion of retorted shale occurred immediately after pyrolysis. For this range of particle sizes, 300–425 μm , AP24 char combustion is distinctly not first order, in agreement with our previous report.[11] Figure 7 shows that our initial rate constant for AP24 char combustion at 475°C is approximately 0.1 s^{-1} . A rapid rate persists for the first 75% of combustion, and then the rate constant falls to 0.012 s^{-1} ; the time for 98% char combustion is approximately 3 min. This is less

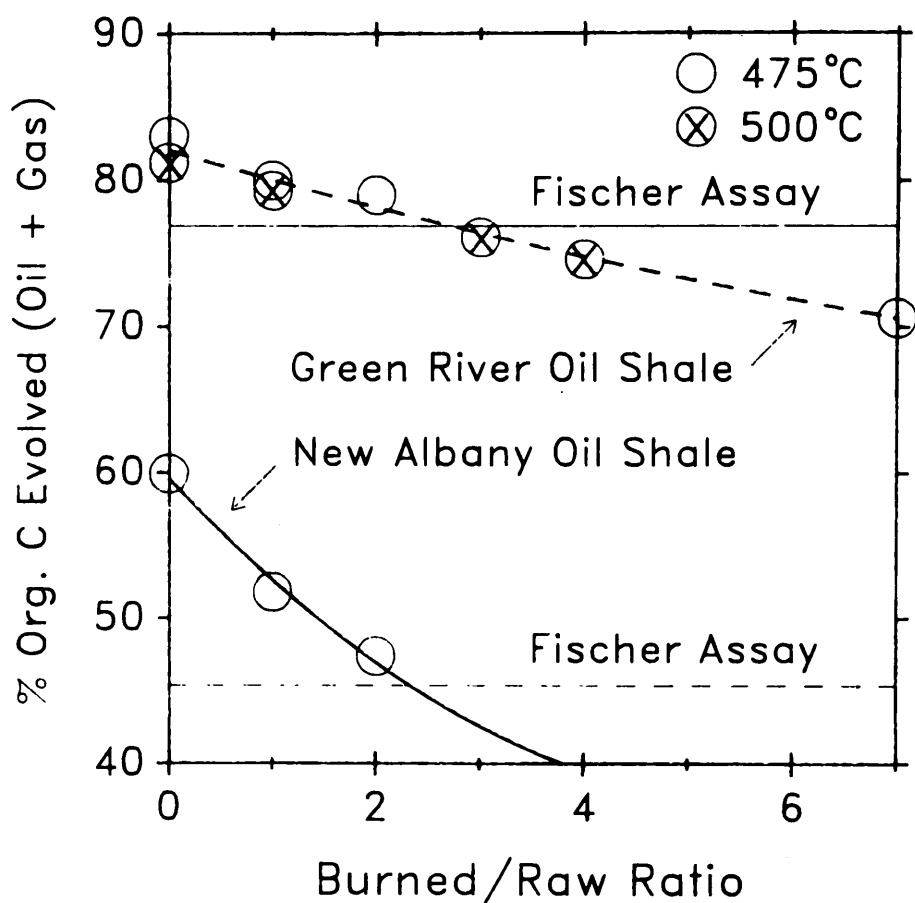


Figure 6. The product yield from pyrolysis decreases as the amount of oxidized shale in the fluidized bed increases. The "burned/raw ratio" is the weight ratio of oxidized shale present in the bed to shale being pyrolyzed.

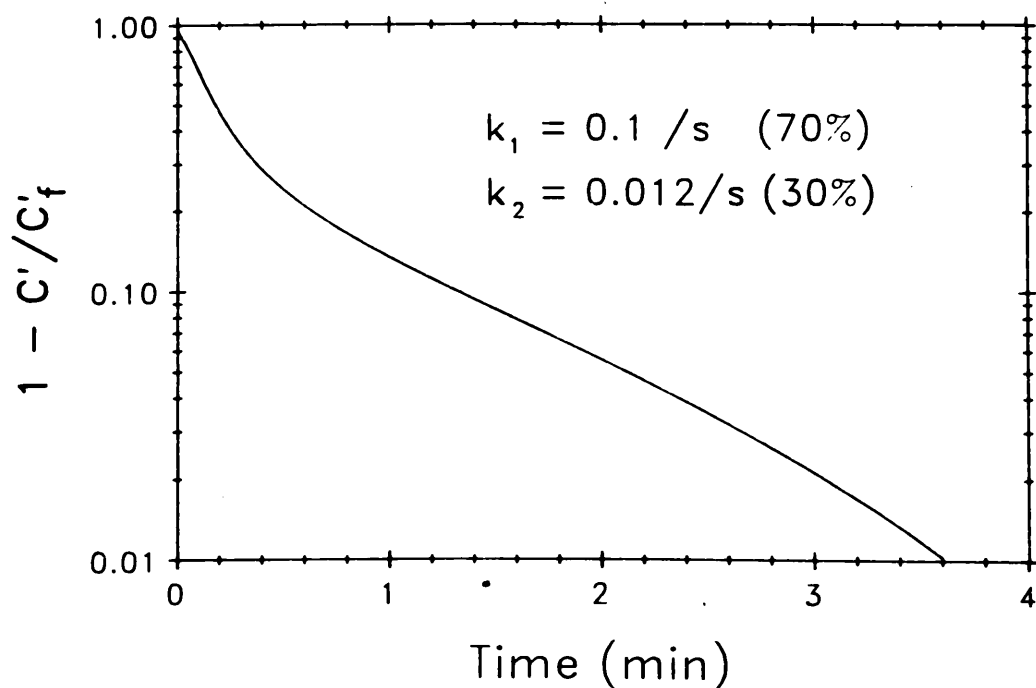


Figure 7. Char combustion at 475°C in 20%-by-volume O_2 of AP24 shale retorted at 475°C. C'_f is the final total amount of C released during char combustion. The process is not first-order.

time than is needed for combustion under these conditions of shale retorted at higher temperatures.[11] The fast-burning fraction of char C decreases with an increase in the burned/raw shale ratio, but the two rate constants remain unchanged.

DISCUSSION

Pyrolysis of AP24 is 98% complete much faster than we previously believed.[5,12] The second rate constant (k_2), which often has been required, is an artifact due to revolatilization and/or secondary product formation in transfer lines or elsewhere and is unrelated to pyrolysis. The time needed for 98% pyrolysis of AP24 shales can be calculated from initial rates constants (k_1) that are widely available for temperatures of interest.[1-5] Our estimate of time required for 98% pyrolysis of Devonian shale is also lower than other work would suggest.[3,6] In our case, the second rate constant is closer in magnitude to k_1 and the tail associated with hydrocarbon release is less important. We concur with Carter that secondary reaction chemistry is responsible for the NA13 k_2 . Engineering design solutions could minimize the impact of k_2 and maximize volatile product yields.

Based on this work, in December 1987, we processed AP24 in our pilot-scale retort at 500°C with a residence time of 1.5 min rather than the usual 3 min. An energy balance consistent with a good yield was obtained. This preliminary evidence points to a potential for doubled throughput with no loss in oil yield. However, oil yields in excess of Fischer assay have not been achieved using the LLNL pilot-scale solid-recycle retort to process either New Albany or Green River oil shales.[12] This is apparently due in part to the action of recycled shale. Oil loss is the result of char formation not gas formation, and the presence of oxidized shale increases the yield of char. Yet, charring does not seem to retard oil release. Over the range investigated here, the rate of oil release was independent of the burned/raw ratio. Work is underway in our laboratory to understand coke-forming activity of processed shale and to develop methods to reduce coking.

The handling of oil shale, particularly processed shale in a fluidized bed, generates dust. Although the mass fraction is small, the specific surface area of dust is so large that it probably plays a role in coking and cracking reactions. For our experiments, we placed a quartz-wool dust filter at the pyrolyzer exit. The amount of dust on this filter and the filter temperature are parameters that we are currently investigating in order to understand better the kinetics for the final few percent of kerogen pyrolysis.

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