

OIL SHALE RETORTING IN DENSE PHASE HOT-SOLID RECYCLE SYSTEMS

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ABSTRACT

Oil shale processing remains primitive despite more than a century of study and development. To expand the industry in China, and to develop an industry in the U.S.A., more efficient, environmentally acceptable oil shale retorting schemes are required. Rapid pyrolysis, solid-recycle retorts offer high throughput and improved oil yield compared to hot gas retorts currently in operation. At the Lawrence Livermore National Laboratory (LLNL), we are studying this class of retort, by combining laboratory and mathematical model development efforts with operation of a 1 tonne/day pilot-scale, solid-recycle retorting system.

In this paper we first discuss hot gas and hot solid retorting methods. We then compare laboratory pyrolysis kinetic and yield results with those obtained using the LLNL pilot retort, processing both Western and Eastern U.S.A. shales. Sulfur chemistry important in solid-recycle retorting is discussed. Based on this experience, coupled with laboratory measurement for shales from Maoming and Fushun, China, we discuss the possibility of processing Chinese shales in rapid-pyrolysis, solid-recycle retorting systems.

INTRODUCTION

The world supply of oil shale is enormous. Oil can be obtained by simply heating the shale to convert the contained organic matter to shale oil. The challenge is to develop processes that efficiently recover this oil at a cost which competes with conventional petroleum technology.

A number of oil shale retorts have operated in the U.S.A. and abroad over the past decades. Virtually all processes consist of two fundamental steps: 1) A preparatory mining (blasting), crushing and sizing step to provide a suitable feed material for retorting and 2) a shale heating step during which the solid organic matter (kerogen) is decomposed producing oil vapor and gas, leaving behind residual organic carbon (char) in the spent shale. Combustion of the char provides the energy to drive the process, with the methods of combustion and for transferring this energy to the raw feed distinguishing the retorting processes.

Hot Gas Retorts

For a century hot gas retorting has been the most wide spread method for transferring heat to the raw shale. In internal combustion retorts, air is injected into a fixed or moving packed bed of shale, burning the char and producing hot gas which is driven through the bed transferring heat to the incoming shale. In external combustion retorts, gas is heated externally, either by burning spent shale or another fuel, and is then piped to the retort. In this way, the combustion and retorting processes are uncoupled, avoiding problems of oil combustion through oxygen

bypass possible in internal combustion retorts. The product gas is typically of low fuel value, and the produced oil yield is equal to or less than that from Fischer assay.

Hot Solid Retorts

The essential feature of this class of retorts is rapid mixing of the raw shale with a solid heat-carrying material. This can heat the raw shale so rapidly that throughput is limited by pyrolysis rather than heat transfer. Oil yield is maximized by rapid removal and condensation of pyrolysis products, avoiding oil loss to coke and gas. Although solids must be circulated, the gas required to move them pneumatically is less than the amount required for heat transfer in hot gas retorts. Also in the case of shales which contain large amounts of carbonate minerals, heat loss due to endothermic decomposition reactions can be largely avoided. Following is a comparison of these two major retort classes.

HOT GAS RETORTS	HOT SOLID RETORTS
Commercial operations High gas-pumping costs Slow heat up (throughput) Nonuniform gas flow a problem Low fuel value product gas Oil yield at or below Fischer assay Mineral decomposition high Flue gas may contain up to half the sulfur in the raw shale	Laboratory & pilot-scale only Low gas-pumping costs Rapid heat up (throughput) Nonuniform gas flow not a problem High fuel value product gas Oil yield above Fischer assay possible Mineral decomposition low More or less sulfur in flue gas depending on mineral content of shale

LLNL PILOT SCALE RETORT

At LLNL, we have constructed and operated a 1 tonne/day pilot-scale solid-recycle retorting system, designed from results of controlled laboratory experiments and mathematical models. Operation of the retort has advanced our knowledge of the chemistry and physics of rapid retorting allowing us to develop new laboratory experiments and make improvements in our mathematical models. In the LLNL system, raw shale is typically mixed with 4 times its mass of 640°C burned shale. Rapid mixing is accomplished by a series of alternating chutes in which the raw shale reaches 500°C within 20 s. From the mixer the solid flows into the pyrolyzer where it is held while the kerogen decomposes. Pyrolysis gas and oil vapor is swept from the retort, through exit ports and is quickly condensed to minimize the formation of coke and gas. The retorted (spent) shale, leaving the reactor, is transported to the top of the combustor by a short lift pipe. Combustion of the residual carbon begins in this lift pipe and continues in the LLNL designed cascading burner, as the solid tumbles down a series of alternating chutes. The final temperature is controlled by adjusting the lateral flow of air across the burner.

Results from the operation of the hot-solid retort have been published by Mallon (1985), Cena and Mallon (1986) and Cena and Taylor (1986). The Fischer assay oil yield and chemical composition of shales used in the LLNL pilot system are given in Table 1. For comparison, shale from Maoming and Fushun, China are also characterized in this table. The Anvil Points shale is from the Green River formation of Western U.S.A. and the New Albany shale is a Devonian age shale from Eastern U.S.A. Note that the organic carbon content is approximately 11 wt% for all the shales except for Maoming, which contains 17 wt% organic carbon.

Operating parameters used to process these two U.S.A. shales, and the results, are given in Table 2 through 4. As shown in Table 2, both shales produced essentially Fischer assay oil yields. This was particularly disappointing in the case of the New Albany shale since laboratory experiments have shown that rapid pyrolysis can give oil yields at least 1.3 times Fischer assay. An explanation of this apparent discrepancy is discussed below.

Table 1. Chemical Analysis of Shales

Percent of Raw Shale	Anvil Points	New Albany	Maoming China	Fushun China
Fischer Assay				
Oil	9.1	5.4	8.3	7.7
Water	1.8	2.4	10.8	6.4
Spent shale	88.	91.	77.	81.
Gas + Loss	1.5	2.0	4.5	4.5
Components				
Org Carbon	11.4	11.1	17.0	11.0
Sulfur	0.6	4.2	1.7	0.7
Nitrogen	0.7	0.2	0.8	0.8

Table 2. LLNL Pilot Retort Results

	Anvil Points	New Albany
Grade (gal/ton)	24	13
Steady State Time (min)	25	38
Raw Feed Rate (gm/min)	762	591
Hot / Raw Ratio	4.2	4.9
Shale Residence Time (min)	4.1	4.7
Raw Feed Temperature (C)	90	19
Recycled Shale Temperature (C)	660	684
Retort Temperature (C)	507	522
Oil (% Raw Org. Carbon)	69	40
Oil (% Fischer Assay Yield)	103	101
Oil Properties		
Carbon (%)	84.7	82.9
Hydrogen (%)	11.1	10.7
Nitrogen (%)	1.6	1.0
Sulfur (%)	0.6	1.8

Table 3.

Mass Distribution % of Raw Feed

	Anvil Points	New Albany
Solids		
Spent Hopper	52	81
Product Cyclone	17	3
Combustor Cyclone	14	5
Gas		
Pyrolysis	2	1
Combustor (Carbon only)	3	2
Oil	8	6
Closure (Out/In x 100)	96	98

Table 4.

Component Distribution % of Raw Feed

	Anvil Points	New Albany
Organic Carbon		
Solids	6	35
Pyrolysis gas	8	7
Combustor gas	17	19
Oil	69	40
Sulfur		
Solids	83	57
Pyrolysis gas	0.5	1
Combustor gas	-	38
Oil	9	3
Loss	7	1

EXPERIMENTAL

Pyrolysis Kinetics

In solid-recycle retorting, raw shale is heated rapidly and the time of isothermal soaking can be closely controlled. Pyrolysis kinetics, important for all retorting processes, is the key factor controlling throughput in solid-recycle systems. Clearly, pyrolysis kinetics must be known accurately for efficient operation of this class of retorts.

Recently Coburn, et al., (1988) have remeasured isothermal-pyrolysis kinetics to more accurately determine both kinetics and yield potential. In that work, the rate of pyrolysis was determined by measuring the concentrations of CO₂ and H₂O in combusted pyrolysis gas. The pyrolysis gas was generated by heating shale in a small laboratory fluidized bed, which was then catalytically burned and measured. The kinetic results, faster than previously thought, for Anvil Points, New Albany and Maoming shale are shown in Figure 1. In the figure, the factor C is the amount of carbon released as a function of pyrolysis time, and C_f is the final amount of organic carbon released during pyrolysis. Thus the fraction of pyrolysis carbon remaining at any time is (1-C/C_f), and the slopes of the curves are proportional to reaction rate constants. Table 5 summarizes reaction rate constants for the three shales at 475°C, with pyrolysis fastest for New Albany shale and slowest for Maoming shale.

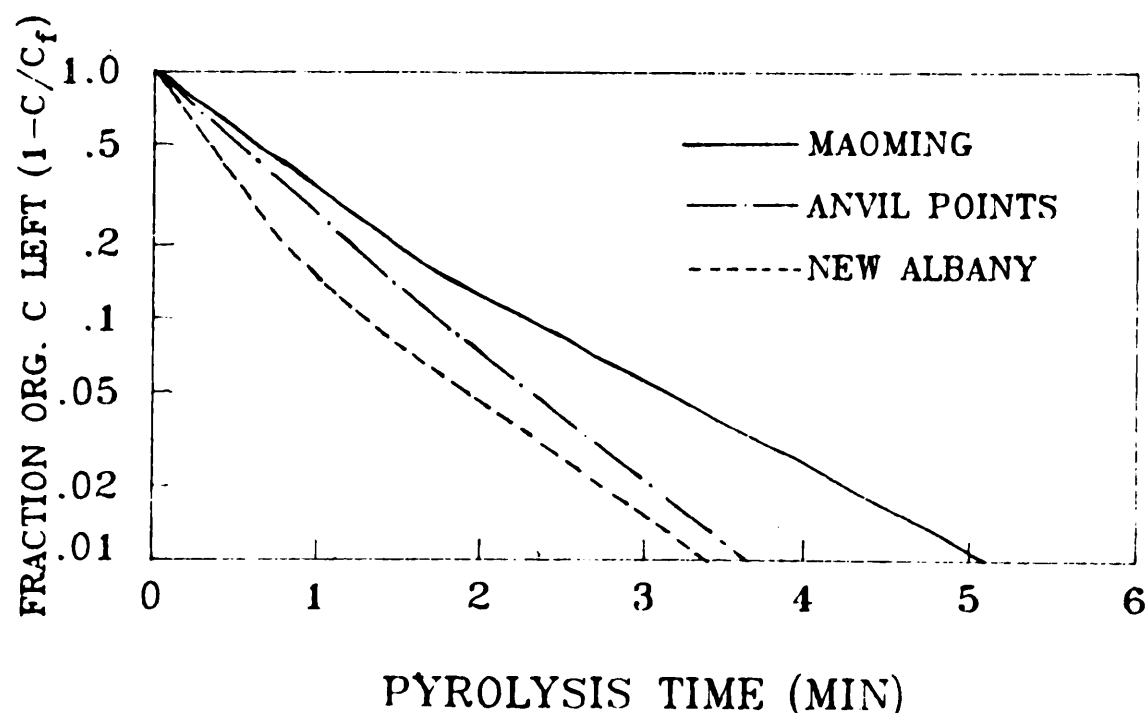


Figure 1. Shale pyrolysis at 475°C Laboratory measurements by a fluidized bed. C is the amount of carbon released as a function of time, and C_f is the final amount of carbon released during pyrolysis at this temperature. The slopes of the lines correspond to the reaction rate constants. Maoming shale has a slower rate of pyrolysis than the other shales.

Table 5.

Pyrolysis Rate Constants at 475°C in Min⁻¹
(first-order approximations)

Shale	K ₁	%	K ₂	%	Time for 98% Pyrolysis (min)
Anvil Points	1.4	90	1.2	10	3.0
New Albany	1.8	90	1.3	10	2.6
Maoming	1.3	84	0.75	16	4.3

Bases on these results extrapolated to 500°C, we calculate that the time necessary for 98% pyrolysis of Anvil Points shale is about 1.5 min at 500°C. This is half the retorting time generally used in the pilot retort (Table 2). We recently operated the LLNL pilot retort taking advantage of this new information. Preliminary analyses show no loss in yield resulted from the shortened pyrolysis time.

Yield Enhancement with Rapid Heating

Another advantage of the rapid pyrolysis retorting is increased oil yield, as shown in Table 6 and Figure 2. We have found that when raw shale is heated rapidly, in a laboratory fluidized bed at approximately 1500°C/min, the yield of oil and gas is increased over that measured during slower heating processes. The combined yield of oil and gas increases by 108% over Fischer assay for Anvil Points shale, and for New Albany and Maoming shales the increase in yield over Fischer assay was approximately 125%. Fischer assay corresponds to a heating rate of 12°C/min. From the data, it appears that when the fraction of raw shale organic carbon recovered by Fischer assay is low (below 60%), significant gain in oil yield by fast heating is possible. The oil and gas recovery of Moaming, Anvil Points and New Albany shales at 2°C/min, and Anvil Points at 2 °C/hr were measured by Burnham (1988). Additional data on heating rate versus yield for Devonian shales is from Coburn and Rubel, 1983, as well as data from and Campbell et al., 1978, for Anvil Points shale.

Table 6.

Percent Organic Carbon Recovered in Oil & Gas Versus Heating Rate

Shale	2 °C/hr	2 °C/min	12 °C/min	1500 °C/min
Anvil Points	63	74	76	82
New Albany	—	43	45	60
Maoming	—	39	42	50

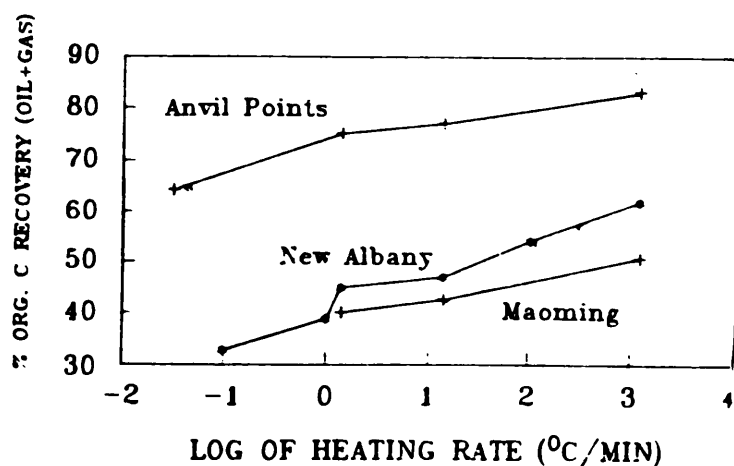


Figure 2. Role of heating rate on yield. The percent of the organic carbon recovered as oil and gas increases as the rate of heating increases. The trend is more pronounced for the shales which have low yields, such as the New Albany Devonian type shale. The yield for Fischer assay are the values given at a heating rate of 12°C per minute.

Effect of Oxidized Shale on Yield

The potential for oil yields above Fischer assay under flash pyrolysis is obvious. However, oil and gas yields from the LLNL pilot retort have not significantly exceeded Fischer assay yields. To explain this we are investigating, in the laboratory, the role of oxidized shale in promoting coke-formation during pyrolysis. In one experimental study, shales were flash pyrolyzed in a fluidized bed which contained various amounts of oxidized shale. The results, presented in Figure 3, show a decrease in oil and gas yield as the relative amount of oxidized to raw shale increased. The effect is most striking in the case of the New Albany and Maoming shales, with most if not all of the enhanced yield potential of flash pyrolysis eliminated at burned to raw ratios as low as 2 to 1. These results confirm the pilot retort results which produced oil yields no higher than Fischer assay, with a burned to raw ratio between 4 and 5 to 1.

Thus it appears that although oxidized shale provides an effective heat carrier in solid-recycle retorting, its presence inhibits attaining the full yield potential of the shale. Factors known to play a role in coke formation are temperature, surface area, chemistry, and contact time. We are investigating the relative importance of each of these variables to optimize retorting parameters and improve yield.

If the research shows that oxidized shale cannot be used directly as a heat carrier for shales subject to coking, one solution would be to heat an inert solid (i.e. ceramic-balls) in the combustor and then circulate it to the pyrolyzer. However, before these alternatives are advanced, a better understanding of the coke forming processes must be determined.

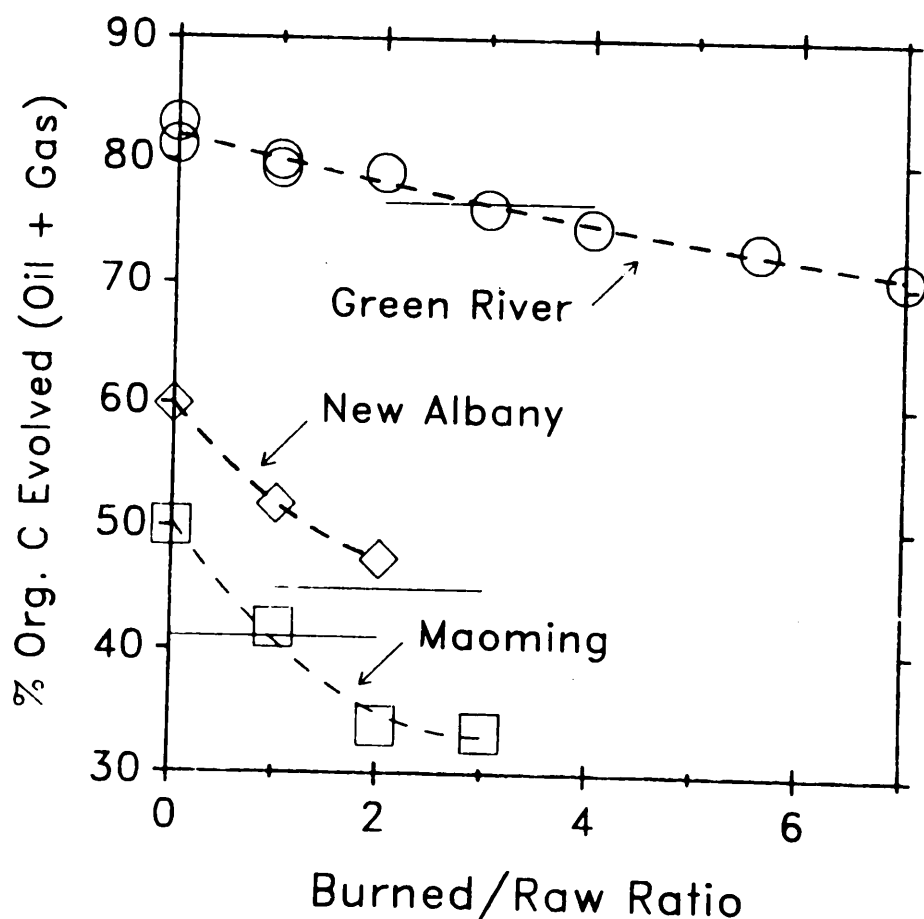


Figure 3. When oxidized shale is present during flash (rapid) pyrolysis the yield decreases. Laboratory data at 475°C from fluidized-bed pyrolysis, Green River Anvil Points, New Albany and Maoming shales. The burned/raw ratio is the weight ratio of oxidized shale in the fluidized bed to the raw shale being pyrolyzed. The horizontal lines show the percent organic carbon recovered during Fischer assay for these three shales.

SULFUR CHEMISTRY

All oil shales contain sulfur, and New Albany and Maoming shales contain more sulfur than Anvil Points shale (Table 1). Shale kerogen contains between 1 and 2 wt% sulfur, and the balance of the sulfur is mostly in the mineral pyrite (FeS_2). The distribution of sulfur is an important factor in shale processing, particularly from the standpoint of air pollution, but it plays a role in heat balance as well.

In hot gas retorting, as with Fischer assay, much of the sulfur is released as H_2S . The distribution of sulfur during solid-recycle retorting, shown in Table 4, is quite different. In this case the oxidized shale in the pyrolyzer captures not only organic sulfur but also sulfur released by pyrite. The capture is by iron oxides to form FeS , which carries nearly all of the sulfur to the combustor. Only trace quantities of H_2S are observed in the pyrolysis gas when processing both Western and Eastern U.S.A. shales. Since the iron oxides are formed in the combustor from FeS , we see that the H_2S emission is self scrubbing and independent of the pyrite content of the shale.

In the combustor, FeS is burned to iron oxides and SO_2 , with the extent of FeS combustion more or less proportional to the fraction of char burned. This potentially represents a significant air pollution problem, however when Anvil Points shale is combusted in the pilot retort, no SO_2 emission occurs. This is due to another scrubbing reaction, this time between SO_2 and the abundant carbonate minerals in this Western U.S.A. shale. Neither New Albany nor Maoming shales contain sufficient carbonate minerals to scrub SO_2 and much of the sulfur would be released as SO_2 as shown in Table 4 for the New Albany case. It may be possible to add an active fine grained limestone or dolomite to the raw shale to capture SO_2 during retorted-shale combustion. We tried dolomite addition with New Albany shale in the LLNL pilot retort. However, due to the large grain size used, and the low combustor operating temperatures, between 600 and 700 °C, too low to drive sulfation reactions, little scrubbing of the SO_2 occurred (Cena and Taylor, 1986).

CONCLUSIONS

Hot-solid recycle systems for retorting oil shale have high throughput, limited by the rate of kerogen pyrolysis. We have measured the rate of kerogen pyrolysis for three shales by means of the same isothermal technique and have found the time necessary for 98% completion at 475°C ranges from approximately 3 min for an Eastern U.S.A. shale to 4 min for Maoming shale from China.

Retorting systems which heat shale rapidly have the potential for high organic carbon recovery. Shales which yield the smallest fraction of their organic carbon to oil and gas during the 12°C/min heating of Fischer assay show the greatest improvement in oil yield when retorted rapidly. The Maoming shale is in this class.

In the LLNL pilot retort organic carbon recovery is about the same as Fischer assay in spite of rapid heating. In this system raw shale is heated by direct contact with hot oxidized shale. We believe the recycled oxidized shale facilitates coke formation at the expense of gas and oil production and thus limits the potential for increased oil recovery.

We are investigating the action of recycled shale on oil yield and have found that shales which

show the greatest improvement in yield with rapid pyrolysis also show the greatest reduction in yield when oxidized shale is present during pyrolysis. We are continuing these laboratory studies to determine under what conditions high yield and throughput are possible in solid-recycle retorting of oil shale.

ACKNOWLEDGMENT

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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