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A MATHEMATICAL MODEL OF FORWARD COMBUSTION RETORTING OF OIL SHALE

By
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Laramie Energy Technology Center
U. S. Department of Energy
Laramie, Wyoming

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TECHNICAL PROGRESS REPORT

A MATHEMATICAL MODEL FOR FORWARD COMBUSTION RETORTING OF OIL SHALE

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PREFACE

In any active mathematical modeling effort the decision to prepare a report describing the current stage of development of the model is difficult, because of the realization that the report will be obsolete before it is printed. Therefore, the normal tendency is to wait until the model is "perfected" before publishing, and "perfection" can, of course, never be fully realized. In an effort to overcome this tendency, this report is being published to introduce and to present the background for a mathematical model of vertical, forward combustion retorting of oil shale which is being developed by the Department of Energy at its Laramie Energy Technology Center in Laramie, Wyoming. As necessary data become available and model accuracy improves, this initial Technical Progress Report will be followed by other publications presenting updates and the completed user-oriented code.

This modeling effort was started in early 1970, shortly after a 150-ton oil shale retort was put into operation at the Laramie Energy Technology Center. The primary goal of the effort was to develop a better understanding of both the physical and chemical phenomena occurring during the retorting process and to delineate areas in which insufficient data were available, thereby helping to direct the overall research program. An accurate model could be used to define and limit the experimental program, potentially lowering overall costs of the research program.

During the formulation of the model it became evident that some necessary information was either unavailable or of insufficient accuracy to adequately describe the phenomena occurring during the retorting process. Therefore, experimental programs were initiated to develop the necessary data, and the level of the modeling effort was reduced until such time as these data became available. These data are now becoming available, and consequently the modeling effort is being increased.

This report describes a "base model" as developed through 1974 under an in-house effort. Subsequent development work is presently being done under contract with the University of Wyoming. The first phase of this contractual work is nearing completion and the results of this effort should be published in the near future.

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A MATHEMATICAL MODEL OF FORWARD COMBUSTION RETORTING OF OIL SHALE

by

Leroy Dockter[1] and H. Gordon Harris[2]

ABSTRACT

This report describes the first version or "base model" of a mathematical model of vertical, forward combustion retorting of oil shale that was developed through 1974 at the Laramie Energy Technology Center in Laramie, Wyoming. The model was written to simulate conditions and processes occurring in LETC's experimental batch-type 150-ton retort. Information presented deals with the reasoning and justification for developing the model, a description of the modeling effort, and a comparison of the yields, retorting rates, and other information obtained from the model as compared to actual results from the 150-ton retort. Good qualitative agreement between the "base model" and actual experimental results is found. However, quantitative agreement is not realized in this version of the model; some reasons for this are discussed. Current and future work on the model are also discussed.

INTRODUCTION

Increasing attention is being focused on development of commercially competitive processes for recovering oil from oil shale. In view of potential reserves, estimated at more than 1×10^{12} barrels of oil in Colorado, Utah, and Wyoming alone, future utilization of this resource appears inevitable.

Oil shale contains no oil, but rather kerogen, a solid organic substance which is insoluble in typical petroleum solvents. Processing of the shale is thus required to form and release the oil and other light hydrocarbons. It may ultimately prove feasible to recover and utilize kerogen by processes such as solvent extraction, biological action, or chemical treatment. However, the only viable method now available to extract the kerogen from oil shale is through retorting, i.e., by simply heating the shale to a sufficiently high temperature to thermally decompose the kerogen to oil.

Technology for aboveground retorting of oil shale is currently under development by private industry. Several methods are employed to effect

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the required heat transfer (3,4,14).[3] However, there are significant problems in aboveground retorting of oil shale, including very large-scale solids handling and treatment requirements, the necessity to dispose of large quantities of spent shale, high water requirements, and large capital investment for mining equipment and retorting plant facilities.

An alternative to aboveground retorting is offered by in situ processing. Excellent reasons can be advanced for exploring such techniques for processing oil shale. In addition to minimization of solids handling and disposal, it may be possible to economically exploit deep or thin seam deposits of shale. Further, capital investment and water requirements are expected to be lower than for aboveground methods.

For these reasons, work on oil shale at the Laramie Energy Research Center has concentrated on development of in situ technology. A major effort has been directed at vertical retorting techniques, most of which has been centered on forward combustion retorting. The broad objective of the work described in this report was the development of a mathematical model of vertical, forward combustion retorting of oil shale.

BACKGROUND

Although work has been limited, some attempts have been directed toward developing mathematical models of the overall retorting process, or of certain of the more important steps.

Fausett (7) employed a quasi steady-state approximation adopted from classical flame propagation theory to describe the propagation of the high temperature combustion zone through the retort. Analytical expressions for temperature distribution and oxygen concentration were obtained in the form of nonlinear integral equations and a numerical method was developed to evaluate the equations. In addition, a procedure was given whereby the kerogen decomposition model of Fausett could be combined with the temperature profile to give a global model of the oil shale retort. While this retorting model represented qualitatively some features of the retorting process, and gave a good estimate of the oil yield in one case, quantitative agreement between actual and predicted temperature distribution was poor.

Another global model has been described by researchers with the Mobil Research and Development Corp. (11,12). First, a retorting heat transfer model was employed to estimate the air and recycle gas flow ratios and resulting time-temperature profiles within the retort. While a number of important variables were incorporated into the model, it did not predict the shale oil yield because it did not include the multi-reaction kinetic scheme necessary to establish the conversion of kerogen

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

to its various decomposition products. An estimate of the shale oil yield was obtained by superimposing a model for kerogen decomposition on the heat transfer model. However, substantial uncertainty was involved because of lack of knowledge of gas contact and oil recovery efficiency. Further, an adequate description of this model is not available in the open literature because of the proprietary nature of the work.

A process simulation model for oil shale retorting has also been developed by Occidental (15). However, once again this work is proprietary and little public information is available.

Additional recent modeling efforts include those of Sohn (17), Nuttall (16), and Braun and Chin (1). The first described an overall strategy for modeling the Lawrence Livermore Laboratory's "RISE" concept, whereas the second was developed for comparison with fairly small scale experimental retorting studies conducted by Sandia Laboratories. The last and most recent model is the most complete and is the latest effort for modeling the Lawrence Livermore Laboratory's "RISE" concept. While these models were reported to give good comparison for certain of the retorting steps, a detailed description of each was not available at the time the model described herein was being developed, and they have not been applied to results from the 150-ton retort.

Forward Combustion Retorting of Oil Shale

In forward combustion retorting of oil shale an oxidizing gas is forced through the fractured or rubbled oil shale with motion of the flame front in the same direction as the gas flow. It is convenient to divide the retorting process into several zones, identified by the principal mechanisms which occur in these regions, as is shown in figure 1. In the first zone, injected air (with recycle gas, if used) flows through the spent shale where it is heated by unsteady-state heat transfer from the cooling shale. The hot gas next passes to the combustion zone where oxidation of carbonaceous material occurs. Depending on conditions, either oil and gas or residual carbon may be burned, although combustion of residual carbon is preferred. If oxidation of residual carbon occurs, it proceeds as a result of diffusion of oxygen from the bulk gas stream inward through the retorted shale particles, with simultaneous outward diffusion of combustion products. In addition to combustion, carbonates decomposition also occurs in this zone, with liberation of carbon dioxide. Because these decomposition reactions are endothermic, they are important in the overall energy balance for the process.

Leaving the combustion zone, the hot gases next pass to the retorting zone, where kerogen decomposition occurs. As the gases flow through this zone they are cooled by the partially retorted and/or raw shale. The oil, gas, and water formed during kerogen decomposition are then carried along with the retorting gas into another heat transfer zone, where the gases are further cooled by raw shale. Some water and hydrocarbon condensation may occur in this zone.

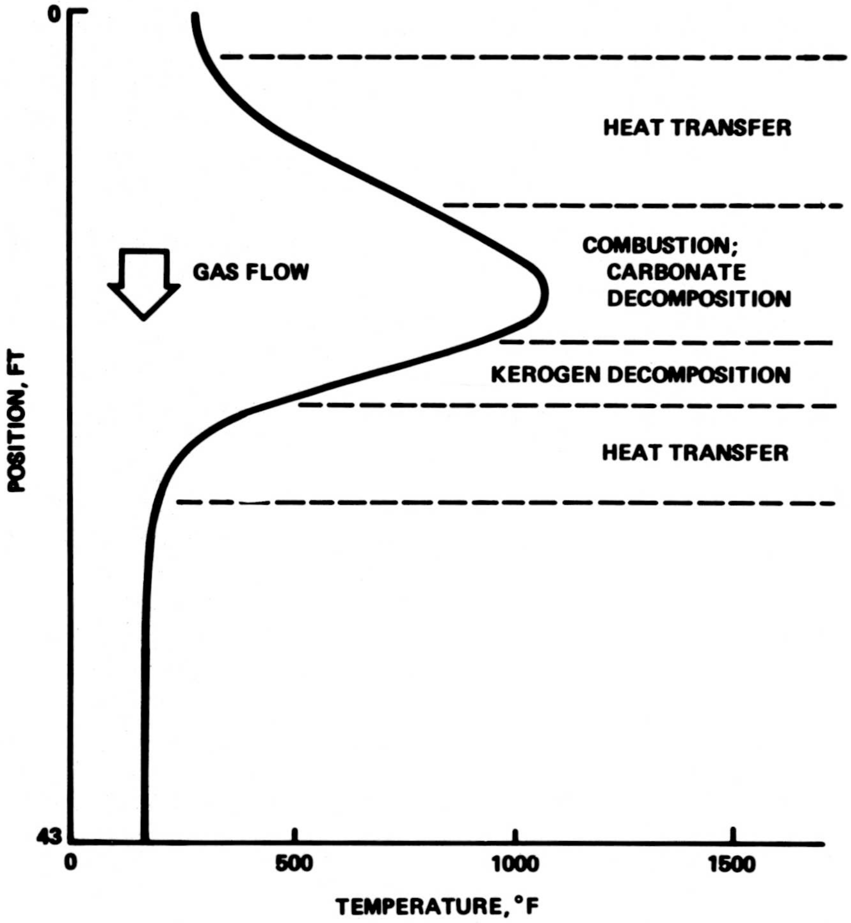

FIGURE 1. - Forward combustion retorting of oil shale

As can be seen from this discussion, a variety of complex physical and chemical phenomena occur in the overall retorting process. A variety of data are thus required as input to a mathematical model. Unfortunately, knowledge of certain of the underlying physical and chemical phenomena is imperfect, and substantial additional research will be needed before the retorting process is clearly understood. Nevertheless, very useful information about the forward combustion retorting process can be gained by employing currently available parameters in a model.

LETC 10- and 150-Ton Retorts

As noted above, most of the experimental work on oil shale at the Laramie Energy Technology Center has been directed toward vertical, forward combustion retorting of oil shale. In addition to extensive laboratory and small-scale pilot data, vertical forward combustion retorting has been carried out in a 10-ton pilot-scale batch retort and a much larger 150-ton batch retort. The overall objective of this experimental program has been to demonstrate the feasibility of forward combustion retorting of randomly sized, mine-run shale, i.e. the type of retorting that would most likely be employed in a vertical, in situ chimney retort. The results of this experimental program have been described elsewhere (5,9); only the major findings will be reviewed here.

The 10-ton unit is a cylindrical vessel 12 feet high with an internal diameter of 4½ feet. The variables studied in the 10-ton unit have included: (a) Shale grade, (b) gas velocity, (c) oxygen content of retorting gas, and (d) particle size distribution. Maximum particle size used in the 10-ton unit has been 20 inches. To date approximately 52 experimental runs have been completed, and work is continuing. These studies have indicated that retorting of randomly sized shale is indeed feasible, with oil yield from lean oil shale (14-16 gallons per ton) ranging from 32 to 56 percent of Fischer assay, while the recoveries from rich shale (20-30 gallons per ton) range from 70 to 80 percent of Fischer assay.

Based on the initial successful results from the 10-ton retort, work was initiated in a 150-ton retort, in which in situ processing could be much more closely approximated. The retort vessel is a refractory-lined carbon steel shell, 45 feet high and 11½ feet I.D.; other design features of the 150-ton retort are similar to those of the 10-ton retort. Figure 2 is a schematic diagram of the 150-ton retort system. The unit has been used to process oil shale ranging in grade from 13 to 35 gallons per ton. The oil shale used in the experimental program consists of

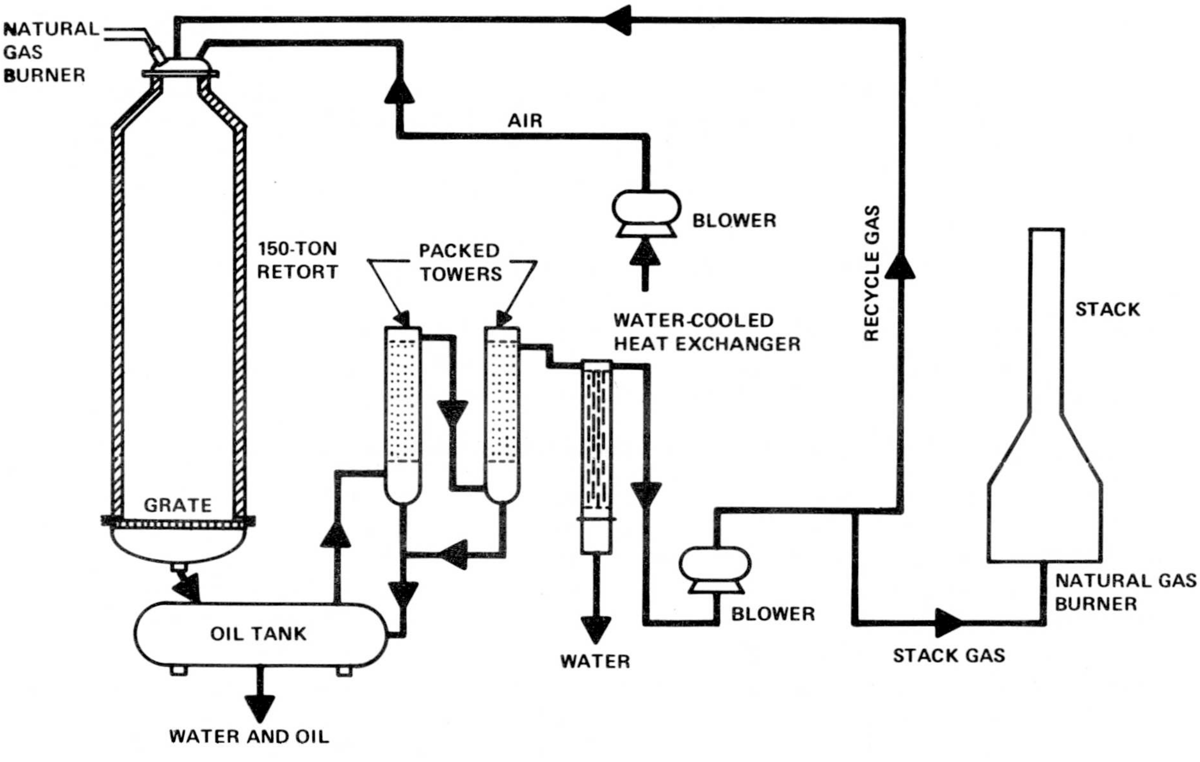

FIGURE 2. - Schematic diagram of 150-ton retort system

mine-run shale, mostly from the Anvil Points facility near Rifle, Colorado. Typical size distribution is shown in Figure 3 (9), although

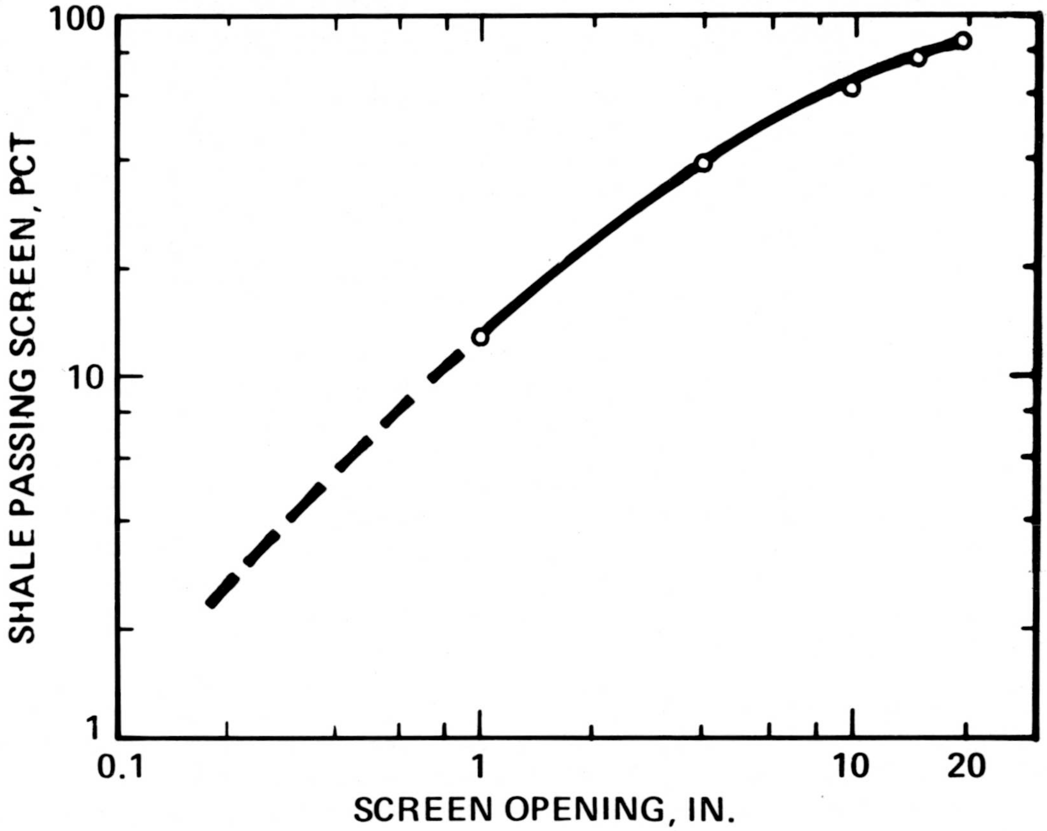

FIGURE 3. - Particle size distribution

several runs were made when the charge included a large piece of oil shale, ranging in size up to 10,000 pounds. Sixteen experiments have been completed to date, and work in the 150-ton retort is ongoing.

Operation of these retorts is straightforward: (a) The retort vessel is charged with shale, (b) the shale is ignited at the top by heating with a natural gas burner, (c) following ignition, air and recycle gas are adjusted to give the desired superficial gas velocity and oxygen content, and (d) combustion proceeds until the combustion front reaches the bottom of the retort. Typical results from the 150-ton retort are shown in Table 1, which gives the results of a set of experiments statistically designed to investigate the effects of the two primary operating variables, superficial gas velocity and oxygen content. Again, feasibility of retorting mine-run shale was demonstrated, with a maximum recovery of 66 percent of Fischer assay for this series of tests (9).

TABLE 1. - Oil recovery in the 150-ton retort, volume percent of Fischer assay

Superficial gas velocity, scfm/ft^2	Oxygen content, volume percent		
	9	15	21
1.25	39	66	54
2.00	-	62	46
2.75	50	62	43

OBJECTIVES

Because of the expense involved in such large-scale experimental work as the 150-ton retort, it became apparent early in the experimental program that development of a mathematical model of the retorting process would be highly desirable. Such a model would prove useful in defining and limiting the experimental program, and would serve as an aid to a better understanding of both the physical and chemical phenomena, and their interactions. The modeling effort would also delineate areas in which insufficient data was available and thereby assist in directing the overall research program.

Accordingly, it was decided to develop a mathematical model of the retorting process, initially to be applied specifically to the 150-ton retort. The objectives of this effort were severalfold: (1) To develop a mechanistic model, incorporating those phenomena which were thought to be most important, (2) to use the simplest approach consistent with a reasonably complete description, (3) to treat unsteady-state, one-dimensional, vertical, forward combustion retorting, and (4) to minimize use of data from the 150-ton retort. The remainder of this report describes the results of this modeling effort through development of a base model for oil shale retorting.

BASE MODEL OF THE 150-TON RETORT

Since the concentrations of the various chemical species and the temperatures in the 150-ton retort vary with both position in the bed as well as with time, partial differential equations are required for description of the retorting process. If a uniform distribution can be assumed over a horizontal cross-section of the retort, only one position variable, the distance from the top of the retort, is required in addition to the time variable. The result is a one-dimensional, unsteady-state problem.

The general approach to the formulation of such equations is to examine a small but finite element at some arbitrary location in the process. Consequently, the bed was divided into N elements, or stages, as illustrated by Figure 4, and unsteady-state material and energy

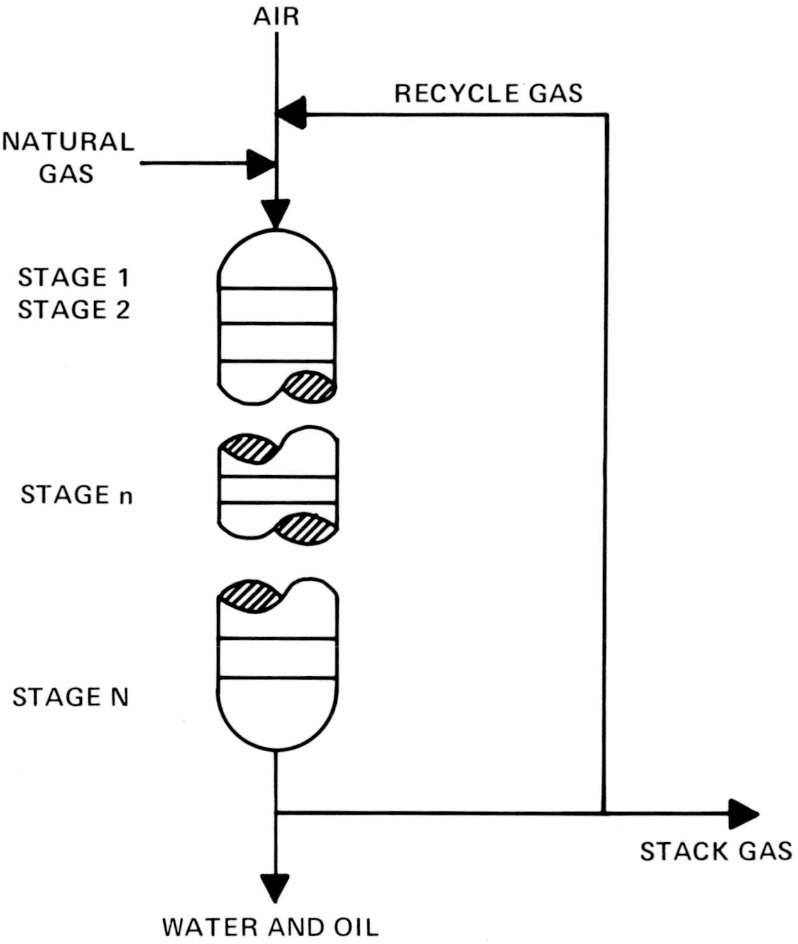

FIGURE 4. - Flow scheme for base model

balances were developed for stage n. These equations are complicated by the fact that retorting occurs in a discontinuous medium, and processes which occur within the shale (kerogen decomposition, carbonates decomposition, and residual carbon combustion) depend on the thermal history of the individual shale particles. For this reason, it was convenient to separate the processes into those which occur in the flowing fluid phases (gas and liquid), and those which occur in the interior of the immobile shale particles.

The overall calculation procedure is that given in Figure 5, which is a simplified computer flow chart for the basic program. The calculation procedure is reasonably straightforward. First the various parameters, vectors, and constants are initialized, and time is incremented. Next, feed gas rate, composition, and temperature are calculated based on inlet air and recycle gas to the retort.

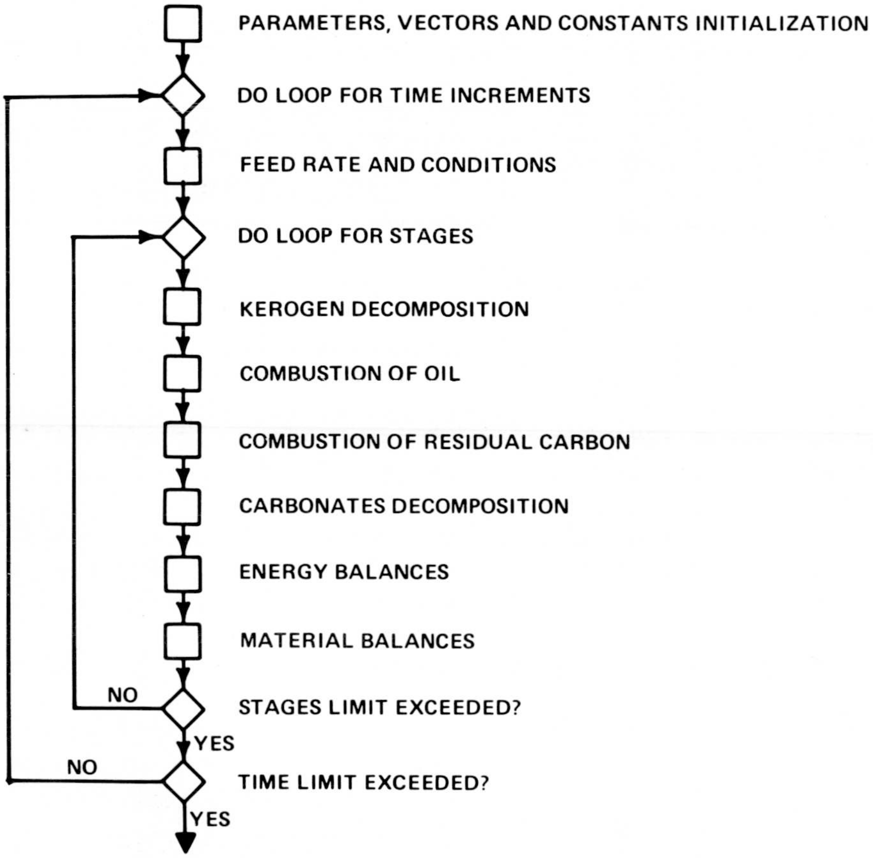

FIGURE 5. - Computer flow chart for main program - base model

In the next step of the calculations the rate and extent of reaction of the following chemical reactions (occurring during the first time increment, in the first stage) are evaluated:

- Kerogen decomposition
- Combustion of oil
- Combustion of residual carbon
- Carbonates decomposition

Based on these chemical reactions, and on physical processes such as heat transfer between fluid and solid phases, energy and material balances are made for the first stage. These computations are then repeated for each subsequent stage, for the first time increment. For each stage, calculation of the physical and chemical processes are based on state properties at the beginning of the time increment, i.e., a forward finite difference technique is employed. Following computations for each stage, exit gas composition and temperature from the retort are known, and recycle gas composition is available for computation of new inlet feed conditions. Time is again incremented, and the entire computational procedure repeated. The computation thus proceeds forward in time until the flame front has been propagated throughout the entire bed.

In the following sections more complete descriptions are given for the material balances for each species (the species continuity equations), the energy balance, and the reaction kinetics.

MATERIAL BALANCES

As noted above, the chemical and physical processes were divided into those which occur predominantly in the solid phase, and those which occur primarily in the fluid phases (gas or liquid). In the base model three principal processes were considered in the solid phase: (1) Decomposition of kerogen, (2) combustion of residual carbon (plus combustion of oil), and (3) carbonates decomposition. In the following three sections, material balances for these solid phase processes will be discussed; in a fourth section material balances on the fluid phase components are covered.

Kerogen Decomposition

Thermal decomposition of kerogen produces shale oil and gas, which are vaporized or flow from the solid shale particles, and an organic coke, which remains in the particle as residual carbon. Additionally, water is released from the shale during pyrolysis. Although not completely valid, a reasonable first approximation is to assume that the oil, gas, and water are released simultaneously as the kerogen decomposition proceeds:

$$\text{kerogen} \longrightarrow \text{oil} + \text{gas} + \text{water} + \text{residual carbon} \tag{1}$$

Terms in the unsteady-state material balances corresponding to decomposition of kerogen in any of the N stages were evaluated by equating the rate of kerogen decomposition to the sum of the rates of formation of oil, gas, water, and residual carbon.

$$-r_{\text{kerogen}} = r_{\text{oil}} + r_{\text{gas}} + r_{\text{water}} + r_{\text{residual carbon}} \tag{2}$$

The rate of formation of oil was obtained from experimental data for the kinetics of kerogen decomposition (discussed later). The rates of formation of gas, water, and residual carbon were expressed in terms of the rate of oil formation in the following manner. The quantities of gas, water, and oil evolved from a known quantity of a particular shale were established by Fischer assay. Subsequent assay of the spent shale gave the weight percent of residual carbonaceous material in the shale. Therefore, the ratio of the mass of gas, water, or residual carbon produced during retorting, to the weight of produced oil was estimated for a particular grade of shale based on Fischer assay. By assuming that the kerogen decomposes according to this fixed distribution throughout the retorting period, the rate of formation of gas, water, and residual carbon was expressed as a fraction of the rate of formation of oil. For example, defining n_{H_2O} as the ratio of water to oil formed as determined from Fischer assay, then

$$r_{H_2O} = n_{H_2O}\, r_{oil} \tag{3}$$

In like manner, each of the terms in equation 2 were evaluated for each of the N stages for production of oil, gas, water, and residual carbon during time Δt.

Combustion Reactions

As kerogen decomposes within shale particles, gas and oil are produced, migrate to the particle surface, and flow downward due to the combined effects of gravity and the sweeping motion of the retorting gases. If oxygen is present and the temperature is sufficiently high, the combustible components of the gas and oil produced will burn. Further, if all the kerogen present has decomposed, no gas or oil is present, and the temperature is sufficiently high, oxygen will react with residual carbon remaining in the retorted shale. The combustion reactions considered were thus:

$$\text{oxygen} + \begin{bmatrix} \text{gas} \\ \text{oil} \\ \text{carbon} \\ \text{residue} \end{bmatrix} \longrightarrow CO_2 + CO + H_2O \tag{4}$$

Since only about 10 percent by weight of the kerogen is converted to gas and only about 60 percent of this gas is combustible, the effects of shale gas combustion were neglected in this base model.

The weight of oil available for combustion in a given stage during time Δt was calculated by adding the quantity of oil produced in that stage in Δt, to the amount that flows in from the previous stage; oxygen available for combustion was obtained from the gas phase material balance. For the purposes of the base model, it was assumed that reaction between oil and oxygen is instantaneous and complete, provided the temperature is sufficiently high. This latter condition is normally met in this base mode for those stages where both oil and oxygen are present. Therefore, the extent of combustion in a given stage depends on the mass of the limiting reactant in the stage. The oxygen required per unit mass of oil was calculated based on the C/H ratio of the oil.

If more oxygen is present in a given stage during time Δt than is necessary for complete combustion of the gas and oil in the stage, then combustion of residual carbon must be considered. The quantity of oxygen available for residual carbon combustion in a given stage was obtained by subtracting the quantity required to burn the oil from the total quantity of oxygen flowing into the stage during time Δt. Experimental data obtained from the 150-ton retort, as well as data from smaller scale retorting equipment indicate that the following observations must be included in the description of the residual carbon combustion process:

a. Due to the physical inaccessibility of the interior of the shale particles, not all of the residual carbon is burned, and combustion occurs via an unreacted core shrinking mechanism.

b. Incomplete combustion occurs, as evidenced by the production of carbon monoxide in the retort.

c. Significantly larger amounts of water are produced than would be expected solely from the Fischer assay analysis.

Although other interpretations are possible, the observations can be explained as the result of the reaction between oxygen and the carbonaceous residue in the shale. The overall reaction can be represented by:

$$\text{oxygen} + \text{carbon residue} \longrightarrow CO_2 + CO + H_2O \qquad (5)$$

Individual reactions that are considered in the base model are:

$$\begin{aligned} C + O_2 &\longrightarrow CO_2 \\ C + 1/2\ O_2 &\longrightarrow CO \qquad (6) \\ H_2 + 1/2\ O_2 &\longrightarrow H_2O \end{aligned}$$

Although additional reactions may occur, such as those involving carbon dioxide or water with residual carbon, they were thought to be of relatively less importance and were not considered in the base model. The number of moles of carbon dioxide, carbon monoxide, and water that resulted from the combustion of residual carbon were expressed in terms of experimentally defined parameters: (1) The C/H ratio of the carbonaceous residues, and (2) the ratio of CO/CO_2 formed from combustion of carbonaceous residues at retorting conditions.

The rate of combustion of residual carbon is discussed in a later section on reaction kinetics. However, by combining this rate with the calculated distribution of carbon dioxide, carbon monoxide, and water, the rate of formation of each of these products was established. The rate of oxygen consumption as a result of residual carbon combustion was thus fixed by stoichiometry. Thus, total oxygen consumption in a given stage in Δt is that due to combustion of oil and residual carbon.

Finally, it was experimentally observed that oxygen was present in the product gas stream of the 150-ton retort for all runs, with oxygen concentration dependent on run conditions. This is undoubtedly a result, at least partially, of channeling and non-ideal flow patterns in the retort, phenomena which could not be easily considered in the base model. Consequently, the fraction of oxygen which was not available for combustion was empirically correlated with inlet oxygen concentration and superficial gas velocity, and only that fraction of the inlet oxygen actually active in combustion was considered in the stage-to-stage calculations.

Carbonates Decomposition

Significant decomposition of carbonates, primarily $MgCO_3$ and $CaCO_3$, was evident at most retorting conditions. This was indicated by high carbon dioxide concentrations in the product gas and by the analysis of inorganics in the spent shale. The kinetics of carbonates decomposition have been studied by Jukkola, et al. (13), as discussed in a later section. The experimental rate equations obtained from these kinetic studies were used in this base model to calculate the rate of carbonates decomposition during time Δt by employing the conditions of temperature, pressure, and decomposable carbonates present in the appropriate stage.

Fluid Phase Constituents

The primary components of the gas stream are inerts, carbon dioxide, carbon monoxide, oxygen, water vapor, and light hydrocarbon gases. Material balances for these components in a particular stage were obtained by accounting for the flow of each component to or from the stage, and the quantity of the component produced or consumed in the stage during time Δt. For example, the carbon dioxide produced in a particular stage by combustion of oil, combustion of residual carbon, and carbonates decomposition was calculated in conjunction with the solid phase reactions. This quantity was simply added to the flow rate of carbon dioxide entering a stage to obtain the amount of carbon dioxide entering the next stage. A similar procedure was followed for carbon monoxide, oxygen, and water vapor. Mass flow rate of inerts through the retort was constant, since there is no net production or consumption of these constituents in the retort.

Flow rate of liquid oil was determined in a similar fashion, based on rate of production from kerogen decomposition and rate of consumption as a result of combustion. Water flow rate was calculated based on condensation from the vapor phase.

REACTION KINETICS

A description of the kinetics of the various reactions which occur is required for both energy and material balances. In general, the approach used was to minimize the overall complexity of the base model by using the simplest and most straightforward technique available for describing the kinetics of the relevant reactions. Kinetic expressions were required to describe kerogen decomposition, the combustion of residual carbon, and decomposition of carbonates.

Kerogen Decomposition

A variety of kinetic schemes of varying complexity have been used to describe the decomposition of oil shale (2,7,8,10). To date, however, no technique appears to be completely satisfactory over the entire range of retorting conditions, and substantial additional experimental and theoretical work remains to be done before a complete understanding of oil shale pyrolysis is available. In any event, the decomposition of kerogen appears to be reasonably well represented by simple first order kinetics, and the following expression was used to describe the kerogen decomposition:

$$r = k_k w_k \tag{7}$$

where: r = rate of production of oil

w_k = mass of kerogen

$\log_{10} k_k = \alpha_k - \beta_k / T$

α_k, β_k from data of Hubbard and Robinson (10)

Combustion of Residual Carbon

Perhaps the most important reaction, from the point of view of overall efficiency of the process, lies in combustion of the residual carbon. This material serves as a primary fuel to sustain the retorting process, and efficient utilization of this material is required to minimize the undesirable combustion of other hydrocarbons (gas or oil). Combustion of residual carbon is a complicated process, requiring transport of the oxygen to the particle surface, diffusion of oxygen into the particle interior, oxidation of the carbon, and transport of combustion products from the particle interior to the bulk gas stream.

At the time of development of the base model, essentially no data had been published on this specific process; however, unpublished data (18), together with information on other similar processes indicated that the process could be well modeled as a diffusion controlled, shrinking-core process. Accordingly, the following relationship was employed in describing the process.

$$r_c = \frac{k\ R C_{O_2} T^{3/2}}{\sqrt[3]{w_c^o / w_c - 1}} \tag{8}$$

where: r_c = rate of combustion of residual carbon

R = particle radius

C_{O_2} = oxygen concentration

w_c = mass of carbon

w_c^o = initial mass of carbon

k from data of Tihen and Dockter

This model has subsequently been corroborated by more detailed experimental data on combustion of residual carbon in spent shale particles (6).

Decomposition of Carbonates

The final principal reaction, in terms of the overall retorting process, is that of decomposition of the carbonates. This process is important both in terms of material and energy balances; the carbon dioxide involved is an important contributor to overall gas composition, and the endothermic decomposition reactions are very significant in the energy balance. Data have been reported by Jukkola (13) and others for oil shale carbonates decomposition. These can be described reasonably well by first order kinetics:

$$r_i = k_i w_i \tag{9}$$

where: i = $CaCO_3$ or $MgCO_3$

r_i = rate of decomposition

w_i = mass of carbonate

$\log_{10} k_i = \alpha_i - \beta_i / T$

α, β from data of Jukkola, et al.

ENERGY BALANCE

In addition to the material balances for each of the constituents in each of the N stages of the reactor, an energy balance for each stage was also included in the base model. As with the material balance equations, it was convenient to divide the energy balance into a fluid phase and a solid phase balance.

Solid Phase Energy Balance

The solid phase energy balance within a given stage was formed by equating the accumulation of energy within a particular stage during time Δt to the sum of: (1) The net increase in energy due to heat transfer from the gas phase to the solid phase (or the reverse), (2) the energy liberated by the combustion of residual carbon within the stage, and (3) the energy required for decomposition of the carbonates. Heat capacities and other thermal data necessary to make the above calculations are available. Terms not included in this initial base model were those associated with: (1) Heat conduction between stages, (2) vaporization of water and oil, and (3) condensation of oil.

Fluid Phase Energy Balance

The fluid phase energy balance for a particular stage of the retort during time Δt was generated by summing together and setting equal to zero: (1) The gain or loss of energy due to flow of gases and liquids into and out of the stage (convection), (2) the gain or loss of energy as a result of conduction between the solid phase and the gas phase, (3) the loss of energy by conduction from the gas phase to the wall, (4) the increase in energy from combustion of oil, and (5) the energy liberated as a result of water condensation. For simplicity, several less significant terms were neglected: (1) Accumulation of energy in the gas phase, (2) conduction in the gas phase, (3) radiative heat transfer, (4) axial and radial energy dispersion, and (5) oil vapor condensation.

DISCUSSION OF RESULTS

The "base model" for vertical, forward combustion retorting of oil shale described in the preceding sections is successful in qualitatively accounting for the main features of the retorting process. First, initiation of combustion (handled in the computer model by addition of heat to the first stage) does in fact result in generation of a temperature profile, which is propagated through the retort. Further, generation of oil and hydrocarbon gases, water, carbon dioxide, and carbon monoxide yields a stack gas which is similar to that experimentally observed, although calculated concentrations of some of the minor components differ somewhat from observed values at some run conditions. However, in terms of the quantitative predictive ability of the model, there is significant disagreement between calculated and experimental results in three main areas:

1. Computed yields are higher than actual. To illustrate, for the high oil yield experimental runs (cf. Table 1), computed yields are generally about fifteen percentage points higher than yields for the corresponding experimental runs; for the lower yield experimental runs, the discrepancy is somewhat greater.

2. Computed retorting advance rate is more rapid than actual. For example, the experimental retorting advance rate for run 2, one of the high oil yield experimental runs, is 1.75 inches per minute, whereas 2.5 inches per minute is predicted by the model.

3. Peak temperatures predicted by the model for the high oil yield experimental runs are consistently about 75° F higher than actual experimental results, and the computed temperature profiles are somewhat narrower than those observed experimentally.

Each of these factors are thought to be closely related, and are probably the result of several inadequacies in the base model. First, considerable non-uniformity of the flame front caused by non-ideal (i.e., non-plug) flow behavior in the retort has been noted experimentally. This may result in incomplete retorting of the shale, thereby contributing to the lower oil yield observed experimentally. No allowance for this phenomenon was included in the base model. Also, the combustion of a larger fraction of organic carbon in an actual run than is accounted for by the model may contribute both to the lower oil yields and slower retorting advance rates observed experimentally. Several factors may be involved in causing this difference, including:

1. In the base model a complete account of particle size distribution was not attempted, although several particle sizes were employed in the calculation of kerogen decomposition rates. In actual runs particle sizes vary over a rather wide range, and differential retorting rates, along with other physical and chemical phenomena resulting from particle size variation, could lead to increased organics combustion and broadening of the temperature profile.

2. Increased residual carbon in the retorted shale swept by the combustion zone; this could result from a different thermal history than that of the Fischer assay method which was used to estimate residual carbon.

3. Slower kerogen decomposition than that predicted from the model, thereby leaving increased quantities of oil, bitumen, or kerogen remaining in the combustion zone.

4. Relatively slow migration of the oil to the shale particle surface, and subsequent combustion of the oil in the combustion zone.

5. Successive desorption and resorption of oil by the shale as retorting occurs, with resulting higher levels of oil being retained in the combustion zone. Also, cracking and coking of the adsorbed oils with resulting deposition of carbon residues could increase the fuel in the combustion zone.

6. Decreased oil from retorting due to low temperature oxidation along the leading edge of the combustion front.

7. Channeling or bypassing of oxygen past the primary combustion zone followed by oxidation of oil or kerogen in the retorting zone.

This last effect (a mechanism for axial dispersion) may also significantly contribute to a broadening of both temperature and concentration profiles.

CONCLUSIONS

The "base model" of vertical, forward combustion retorting of oil shale discussed in this report shows good qualitative agreement with actual experimental results obtained in the LETC 150-ton retort. However, considerable refinement will be necessary before good quantitative agreement will be realized. Work on the model is ongoing, and many of the effects discussed in the previous section are being incorporated into the model, including a mechanism to better account for particle size distribution, and a mechanism to account for a greater fraction of organic carbon remaining in the combustion zone (as kerogen, oil, or residual carbon). In addition, a systematic review of available data related to these and other factors is continuing in an effort to improve agreement between predicted and observed yields and retorting rates. Future work will include attempts to incorporate two-dimensional phenomena into the model. This work will be discussed in later reports.

REFERENCES

1. Braun, R. L., and R. C. Y. Chin. Computer Model for In Situ Oil Shale Retorting: Effects of Gas Introduced Into the Retort. 10th Oil Shale Symp. Proc., Colorado School of Mines, April 21-22, 1977, p. 166.

2. Braun, R. L., and A. Rothman. Oil Shale Pyrolosis: Kinetics and Mechanism of Oil Production. Lawrence Livermore Laboratory, Report UCRL-75974, 1974.

3. Cook, E. W. Oil Shale Technology in the USA. Fuel, v. 53, 1974, p. 146.

4. Cook, G. L. Oil Shale. Ch. in McGraw-Hill Yearbook Science and Technology. McGraw Hill Book Co., New York, NY, 1974, p. 320.

5. Dockter, L., and A. E. Harak. Scale-Up Comparisons Between 10-Ton and 150-Ton Oil-Shale Batch Retorts. ERDA LERC/TPR-76/2, 1976.

6. Dockter, L., and T. F. Turner. Combustion Rates for Oil Shale Carbonaceous Residue. ERDA LERC/RI-77/4, 1977.

7. Fausett, D. W. Mathematical Study of an Oil Shale Retort. PhD Thesis, University of Wyoming, Laramie, WY, 1974.

8. Finucane, D., J. H. George, and H. G. Harris. Perturbation Analysis of Second-Order Effects in Kinetics of Oil-Shale Pyrolysis. Fuel, v. 56, 1977, p. 65.

9. Harak, A. E., L. Dockter, A. Long, and H. W. Sohns. Oil Shale Retorting in a 150-Ton Batch-Type Pilot Plant. US BuMines RI 7995, 1974.

10. Hubbard, A. B., and W. E. Robinson. A Thermal Decomposition Study of Colorado Oil Shale. US BuMines RI 4744, 1950.

11. Johnson, W. F., D. K. Walton, H. H. Keller, and E. J. Couch. In Situ Retorting of Oil Shale Rubble: A Model of Heat Transfer and Product Formation in Oil Shale Particles. Ms. for oral presentation and publication, AIChE Mtg, Houston, TX, March 1975.

12. Johnson, W. F., and I. H. Timmins. Heat Transfer and Product Formation During the In Situ Retorting of Oil Shale. Paper presented at the ASME Resource Recovery Symp., Albuquerque, NM, March 1975.

13. Jukkola, E. E., A. J. Denilauler, H. B. Jensen, W. I. Barnet, and W. I. R. Murphy. Thermal Decomposition Rates of Carbonates in Oil Shale. Ind. Eng. Chem., v. 45, 1953, p. 2711.

14. Matzick, A., R. O. Dannenberg, J. R. Ruark, J. E. Phillips, J. D. Lankford, and B. Guthrie. Development of the Bureau of Mines Gas-Combustion Oil-Shale Retorting Process. US BuMines Bull. 635, 1966.

15. McCarthy, H. E., and C. Y. Cha. Oxy Modified In Situ Process Development and Up-Date. Colorado School of Mines Quarterly, v. 71, 1976, p. 85.

16. Nuttall, H. E. Mathematical Modeling and Experimental Investigation of Oil Shale Retorting. Presented at 51st Ann. Mtg SPE-AIME, New Orleans, LA, 1976.

17. Sohn, H. Y. Modeling of In Situ Oil Shale Retorting. Presented at First Rocky Mountain Fuel Symp., Brigham Young Univ., Provo, UT, January 1976.

18. Tihen, S. S. Unpublished data. LERC.