

OPERATIONAL CRITERION OF A SPOUTED-BED  
OIL SHALE RETORT

by  
LEROY BERTI

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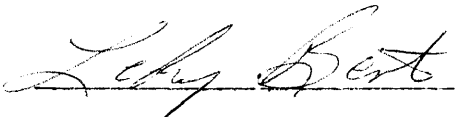
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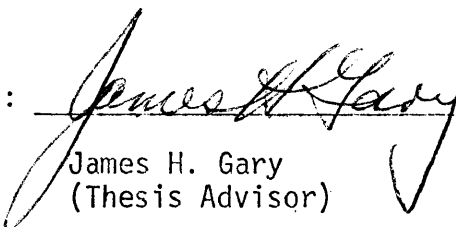
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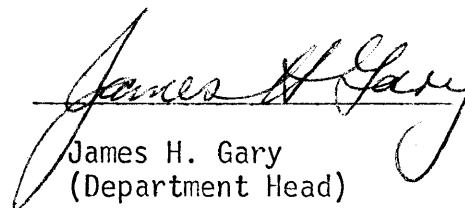
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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical and Petroleum-Refining Engineering.

  
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ABSTRACT

This research is the study of the operating parameters of a pilot-plant-size spouted-bed oil shale retort and the theoretical correlation of them. The difficulty in obtaining accurate measurement of the small oil yields because of oil loss in the recovery system necessitates the use of the air required for combustion as the check between the theoretical correlation and the experimental results. The retort was operated successfully at temperatures between 995 and 1200 °F and at shale feed rates of 10 to 20 pounds per hour with agreement between experimental and theoretical results within experimental error. No attempt was made to correlate operating conditions and the physical operation of the spouting effect.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. James H. Gary for his guidance and encouragement as thesis advisor and to Dr. Anton G. Pegis, Dr. Philip F. Dickson, Dr. Martin E. Fuller, and Professor Elwyn Shimoda for their assistance as thesis committee members. Special thanks are given to John C. Thomas for his invaluable technical assistance.

Acknowledgment is made of the financial support provided by the National Science Foundation and the United States Department of Health, Education, and Welfare.



DEDICATION

This thesis is dedicated to my wife Annette, who endured many hours of loneliness during its preparation, and to my parents for their unending help and encouragement.

## INTRODUCTION

Spouting is a new technique for contacting fluids with granular solids. The spouted bed can be described as a combination of a dilute fluid phase and a coexistent moving, expanded bed (1). Gas enters through an opening at the apex of a conical inlet (Figure 1); this entrance is so abrupt that the gas has no chance for lateral distribution over the total cross section of the shell. This effect forms a central channel of a dilute fluid phase in which the solids are entrained upward. The solids enter the channel mainly from the bottom, but also laterally along the length of the channel. The solids concentration in the channel increases with height, while the outline of the channel becomes less distinct. At the upper end of the channel the solids spill over into the annulus surrounding the central channel. The annulus can be described as an expanded bed in which the particles maintain their relative position as they move downward. The coexistence of these two phases produces a solids flow pattern where the solids are entrained upward in the central channel and descend by gravity in the denser annulus.

Preliminary work on the use of the spouted bed indicated the

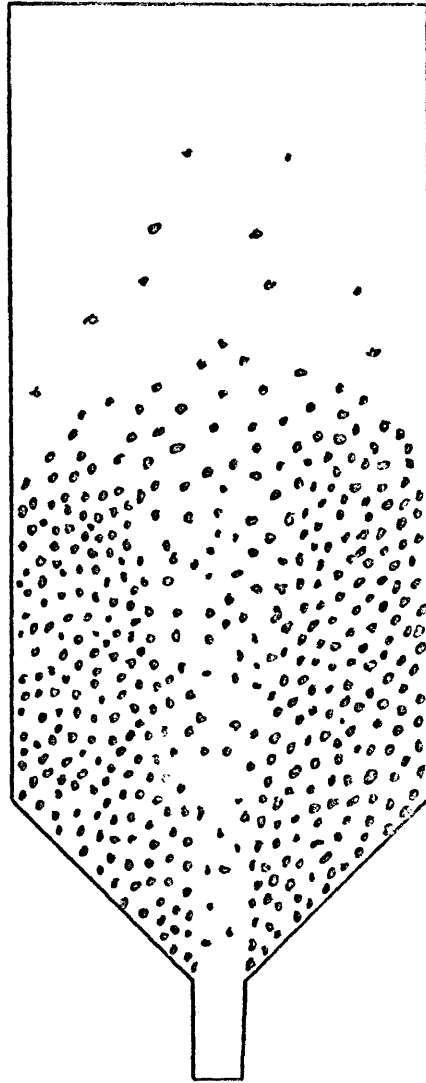


FIGURE 1  
SCHEMATIC OF SPOUTED BED

possibility of its use as an oil shale retort (2). Before major design changes in the reactor vessel and support equipment were initiated, it was desired to obtain a correlation of the operating parameters and the development of a mathematical model to predict responses to changes in operating parameters and also to determine areas for possible improvement of the support equipment. This thesis is the study of these parameters and the development of such a model from an analysis of publications pertaining to the characteristic reactions involved in the retorting operation.

## THEORY

It was necessary to study the kinetics and obtain accurate thermodynamic data for reactions occurring in the system and include these with the sensible heats of the product and feed stream to form a mathematical expression for the heat and mass balance around the reactor.

**OIL SHALE REACTIONS:** Oil shale is a compact sedimentary rock containing organic and inorganic constituents. The organic portion of the shale can be divided into two parts: bitumen and kerogen. The bitumen is considered as the benzene soluble organic naturally present in the raw shale. Kerogen, comprising the remaining portion of the organic matter in the shale, can, by pyrolysis, be converted to a soluble organic, similar to bitumen. Work done by Hubbard and Robinson (3) shows the conversion to the soluble organic to be a first-order process where the rate follows an Arrhenius rate law.

$$\Delta C = C_0(1 - e^{-kt}) \quad (1)$$

Where  $\Delta C$  is the change in kerogen content of the shale,  $C_0$  is the initial concentration of kerogen,  $t$  is time of pyrolysis, and  $k$  is

the Arrhenius rate constant described in the following equation:

$$\log k \times 10^2 = \frac{-5549}{T} + 9.16 \quad (2)$$

The above equation, for temperatures above 818 °F, was used because the residence times of particles at temperatures below this are negligible. As the soluble organic is further heated, it is driven from the shale as a vapor, leaving behind a non-volatile residual carbon. The residual carbon is from 2-weight percent for 28-gal-per-ton shale to 4-weight percent for 75-gal-per-ton oil shale (3).

The inorganic material can be classified into two categories: mineral carbonates and other minerals, which are mostly of the silicate family. The percentages of these minerals vary with shale origins; a typical analysis is shown in Table 1. Experimental work (4), yielding data on the decomposition of the carbonates, has shown them both to be first order with respect to the initial concentration of calcite and dolomite. Rate constants for each species were also found to follow an Arrhenius function. Although the decomposition is complex, a value of 57,000 Btu per mole of carbon dioxide liberated was determined by Dannenburgh and Matzick (5) for the decomposition of the carbonates. They also found that the reactions of the remaining inorganics did not affect heat balances at operation conditions.

TABLE 1- Mineral Composition of Green River Oil Shale (5)

Mineral	Formula	Weight Percent
Dolomite	$(\text{CaMg})\text{CO}_3$	33
Calcite	$\text{CaCO}_3$	20
Plagioclase	$(\text{Na}_x\text{Ca}_y)\text{AlSi}_3\text{O}_8^*$	12
Illite	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$	11
Quartz	$\text{SiO}_2$	10
Analcite	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	7
Orthoclase	$\text{KAlSi}_3\text{O}_8$	4
Iron	Fe	2
Pyrite	$\text{FeS}_2$	1

\* x and y indicate varying percentages

MATHEMATICAL-PROCESS DESCRIPTION: Because this work was conducted to determine the operating parameters of the system and their effect on the system, a mathematical model was developed to analyze the experimental results and to predict responses to changes of these parameters.

The mathematical model was developed from a heat- and mass-balance around the reactor. For analysis, the reactor was considered as a stirred-tank reactor. For determining the kerogen and carbonate decompositions from the individual rate equations, an average residence time was found by dividing the mass volume by the raw shale flow rate. Although there were small temperature gradients, 20 °F in most cases, the reactor was assumed to be isothermal, with the outlet temperature used as the reactor temperature. Although this assumption produced a slight error in the rate constant for the carbonate decomposition, it gave correct values for the sensible heat of the products which had a much larger effect on the heat balance than the carbonate decomposition. The kerogen was decomposed completely during the first 10 minutes of the residence time and was, therefore, completely decomposed at any operational temperature as long as the residence time was greater than this value.

Figure 2 shows the feed streams to the reactor represented by the circles on the left, and the product streams leaving the reactor by the circles on the right. The squares represent theoretical intermediates in the retorting operation with the  $H_i$ 's representing



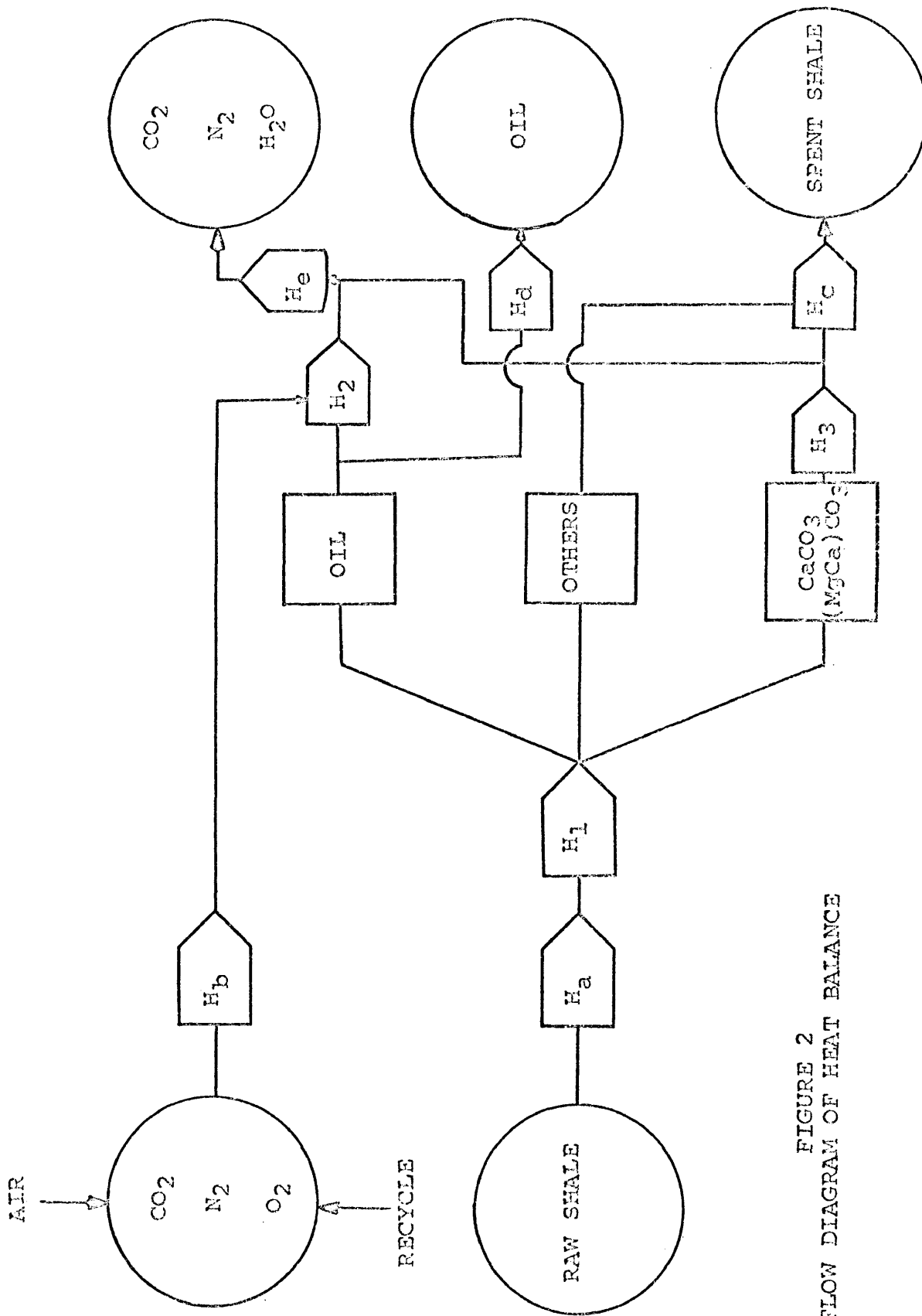


FIGURE 2  
FLOW DIAGRAM OF HEAT BALANCE

heats of reactions needed to form or decompose them. The sensible heats of the products and reactants are represented by the  $H_x$ 's.

The sum of the terms  $H_a$  and  $H_1$ , determined experimentally by Sohns (6) for temperatures to 1100 °F, can be expressed in Btu/lb by the following equation derived from Shaw's work (7):

$$(H_a + H_1) = 0.174 (T_f - T_i) + (0.035 + 0.00081 G) 10^{-3} (T_f^2 - T_i^2) \quad (3)$$

The terms  $T_i$  and  $T_f$  are the initial and final temperatures, respectively, of the shale in °R.  $G$  is the modified Fischer assay of the shale in gal per ton of raw shale. A Fischer assay was not performed on the shale, but 20 gal per ton was estimated from carbon analysis of the shale and weight loss during retorting.

Although Sohns stated his data included the heat of decomposition of the mineral carbonates, the carbonate decomposition at temperatures below 1100 °F is negligible (4) but must be taken into account in addition to Eq. 3 for higher temperatures. The carbonate decomposition was therefore determined from the first-order kinetics. The rate constants for the carbonate decomposition are a function of gas-phase composition as well as temperature. The data for decomposition in a nitrogen atmosphere were chosen because the amount of carbon dioxide is small and because there were no data available for carbon dioxide-nitrogen mixtures. The amount of carbonate decomposition was determined from the kinetic data; from

this the carbon dioxide liberated was determined using the analysis in Table 1. The total carbonate composition, experimentally determined, agreed with the total carbonate in Table 1.

Shaw's publication (7) also gave an expression for the specific heat of the spent shale which gives the following relationship in Btu/lb for  $H_c$ :

$$H_c = 0.174 (T_f - T_i) + 0.026 \times 10^{-3} (T_f^2 - T_i^2) \quad (4)$$

Analysis of the shale on a differential scanning calorimeter (DSC) indicated the value obtained from Eq. 4 for  $H_c$  was very close to the experimental value (Appendix 2). There appear to be some discrepancies in Sohns' work (6) in that he concluded that the heat of retorting ( $H_1$ ) was negligible and analysis of the DSC indicated a significant value. Sohns later stated that there were possible errors in his work and that the heat of retorting was not negligible (8). Work done by Tosco (The Oil Shale Corporation) (9) indicated that Sohns' data were, however, in good agreement with work done on the DSC, and, therefore, Eq. 3 is a good representation of ( $H_a + H_1$ ).

With an approximate specific heat for the oil vapor (10) and a 100-percent oil yield, the value of the term,  $H_d$ , was insignificant.

The terms  $H_b$  and  $H_e$  were easily determined from enthalpy tables (11).

For the calculation of  $H_2$ , the oil product was assumed to have a carbon-to-hydrogen ratio equal to the ratio present in the organic portion of the raw shale. Subtracting the inorganic carbon content from the total carbon content (Appendix 2) gave an organic carbon content of 0.0947 lb per lb shale. With the ratio obtained, a heating value of 16,500 Btu per lb was calculated from the enthalpies and heats of combustion of hydrogen and carbon (12). The calculation assumed that the products formed were only carbon dioxide and water. Gas chromatographic analysis of the vent gas showed no carbon monoxide or light hydrocarbons indicating complete combustion.

Not shown in the diagram is the heat loss from the reactor. The heat transfer from the wall was difficult to calculate because of the effects of the thermowells protruding from the insulation and the irregularity of the surface. An average heat-transfer coefficient at the wall was assumed to be 5 Btu per hr-sq ft- $^{\circ}$ F, giving a heat loss of 3500 Btu per hour.

The heat balance around the reactor was used to calculate the amount of burned organic product.

$$H'_e + H'_c + H'_2 + H'_1 + H'_3 + \text{Loss} - H'_a - H'_b = 0 \quad (5)$$

$H'_i$  is the value obtained when the heat of reaction,  $H_i$ , is multiplied by the extent of reaction as determined from the kinetic expression for each reaction.  $H'_x$  is the value in Btu per hr obtained by multiplying the enthalpies of feed and product streams,  $H_x$ , by their

respective flow rate as determined from the mass balance. Eq. 5 can be rearranged to give the pounds per hour of organic burned as follows:

$$\text{Organic Burned (lb/hr)} = \frac{H'_e + H'_c + H'_1 + H'_3 - H'_a - H'_b + \text{Loss}}{-(H_2)} \quad (6)$$

If the organic is assumed to be 100 percent recoverable as oil, the following equation gives the maximum weight-percent oil yield:

$$\text{Oil Yield} = \frac{(\text{Total Organic}) - (\text{Burned Organic})}{\text{Total Organic}}$$

This yield is hypothetical, for there is always a residual carbon content left on the shale that is not converted to oil products. This yield can be converted easily to one of the empirical yields, such as Fischer assay, for comparisons with other retorting operations by knowing the residual carbon content.

As a check, it was necessary to correlate the data with the mathematical model with one of the process variables. The most desirable variable would have been oil yield, but it was difficult to get reliable, reproducible data. The large physical size of the system masked most of the oil yield because of deposition of oil film in the piping and surge tank. The demister had a tendency to collect oil and flush at sporadic intervals, giving large variations in oil yield.

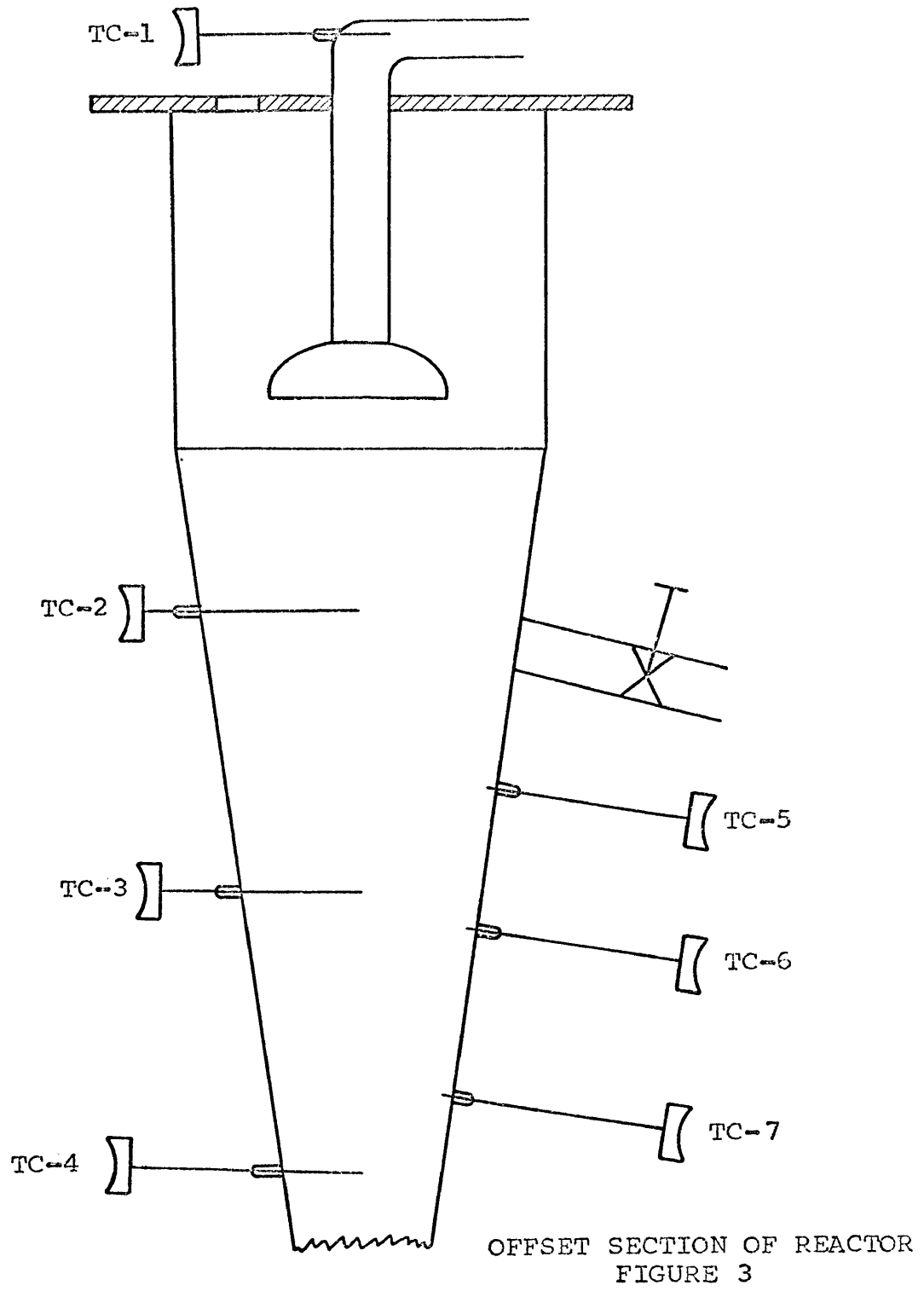
It was necessary to select a variable that was accurately measured and was a true indication of retort operation. The air necessary for combustion met both of these requirements and could be accurately calculated from the mathematical model and from the stoichiometric oxygen needed for the complete combustion of the organic products. The only additional assumption that had to be made was that no excess air was supplied to the reactor. This assumption was justified from the chromatographic analysis of the vent gas on a molecular sieve column showing a very small percentage of oxygen, which was probably due mostly to the air used for feeding the shale.

The spent shale did not provide a very conclusive check because the spent-shale measurement was not very accurate owing to loss in the surge tank; moreover, the relationship of spent shale to raw shale was almost independent of operating conditions in the range of data.

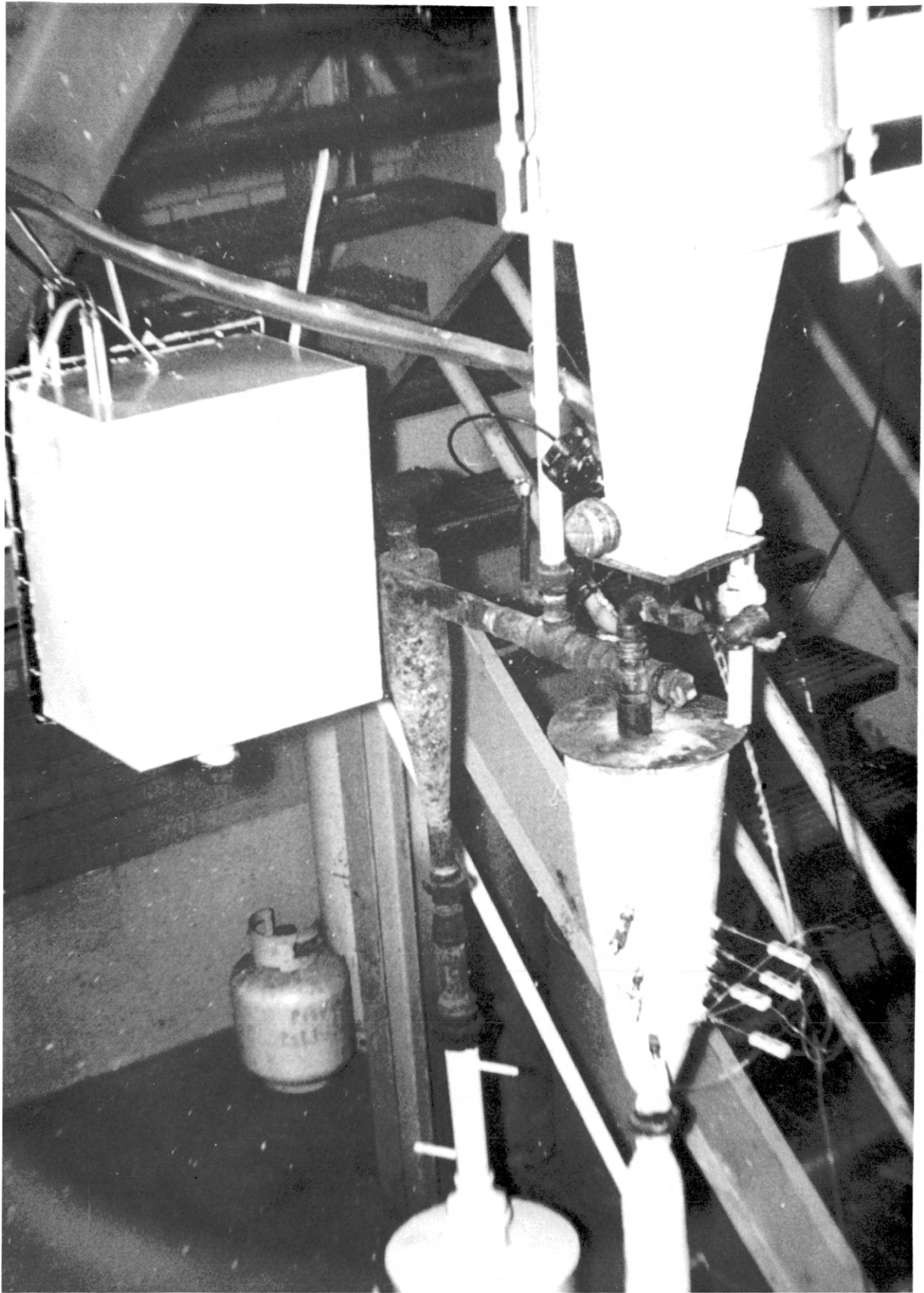
The mass-and-energy-balance equations were solved by programming on a digital computer (Appendix 4). Because the solutions involved trial-and-error calculations to obtain inlet and outlet gas compositions, an iteration technique was used.

EQUIPMENT DESCRIPTION

REACTOR: The reactor is shown schematically in Figure 3. The cylindrical section of the reactor is  $6\frac{1}{2}$  in. in diameter and 6 in. long with a flange welded to the top. The conical section of the retort is  $6\frac{1}{2}$  in. in diameter at the top, tapering to a 2-in. diam. over a length of 18 in. It is welded to the cylindrical section at the top and has a  $1\frac{1}{2}$ -in. pipe nipple 4 in. long welded to its bottom. A top plate, which bolts onto the flange, has attached to it the feeder and the outlet tube. The outlet tube consists of a  $3\frac{1}{2}$ - by  $1\frac{1}{2}$ -in. reducing coupling attached to a  $1\frac{1}{2}$ -in. pipe nipple welded through the center of the top plate. The bottom of the reducing coupling extends 5 in. below the top of the reactor. Material used in the reactor was  $1/8$ -in. mild-steel plate, except for the flange and the top plate which were  $3/8$ -in. mild-steel plate. Quarter-inch pipe nipples were welded into the reactor wall for use as thermocouple mounts. Six such nipples were used: three were mounted perpendicular to the axis of the reactor; the remaining three were mounted orthogonal to these. With linear distances from the flange along the outside of the reactor wall, the nipples were located as follows: 12,  $14\frac{1}{2}$ , and  $18\frac{1}{2}$  in. and 9, 14, and 19 in. A 1-in. pipe was welded







into the side of the reactor 10 in. from the top to facilitate auxiliary solids withdrawal.

**CYCLONE:** The cyclone, 4 in. in diameter, was designed by specifications given in Perry's Chemical Engineers' Handbook (15). It was constructed of 16-gauge mild-steel plate. The spent-shale hopper is a 20-gal drum attached to the bottom of the cyclone by a 4-in. pipe.

**SURGE TANK:** A modified 20-gal transformer drum serves as a surge tank. The rubber seal for the lid was replaced by an asbestos gasket for high-temperature operation. Both gas entrance and exit are axial. The drum is packed with 10 sq ft of  $\frac{1}{4}$ -in. steel mesh. The drum also contains provisions for water-mist nozzles and a water drain to a sealed 55-gal drum.

**DEMISTER:** The demister can best be described as a zero-efficiency axial fan. This is a five-stage unit with axial entrance and tangential exit. Each stage consists of a fan blade, a shim, a flow diverter, and a stage separator. These components are described in a previously published article (2).

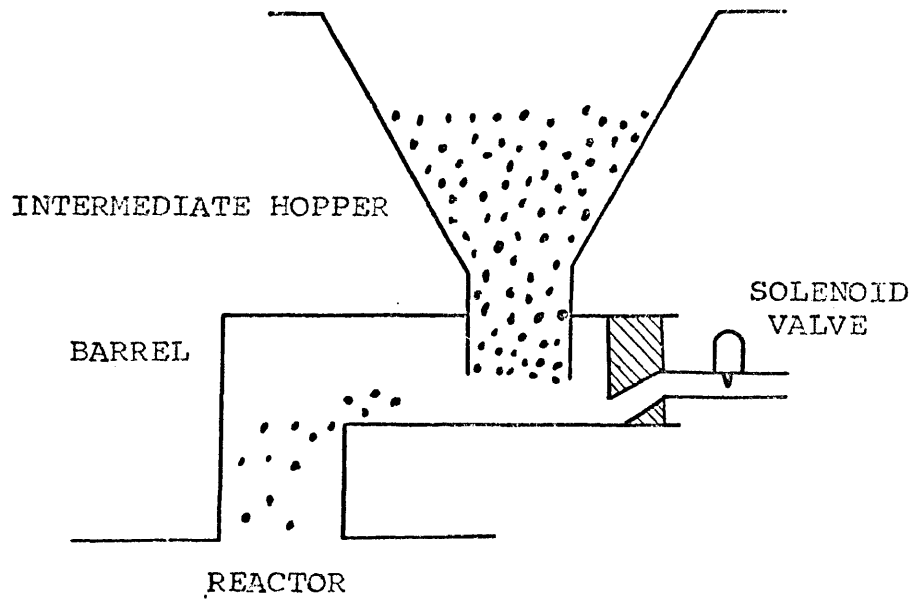
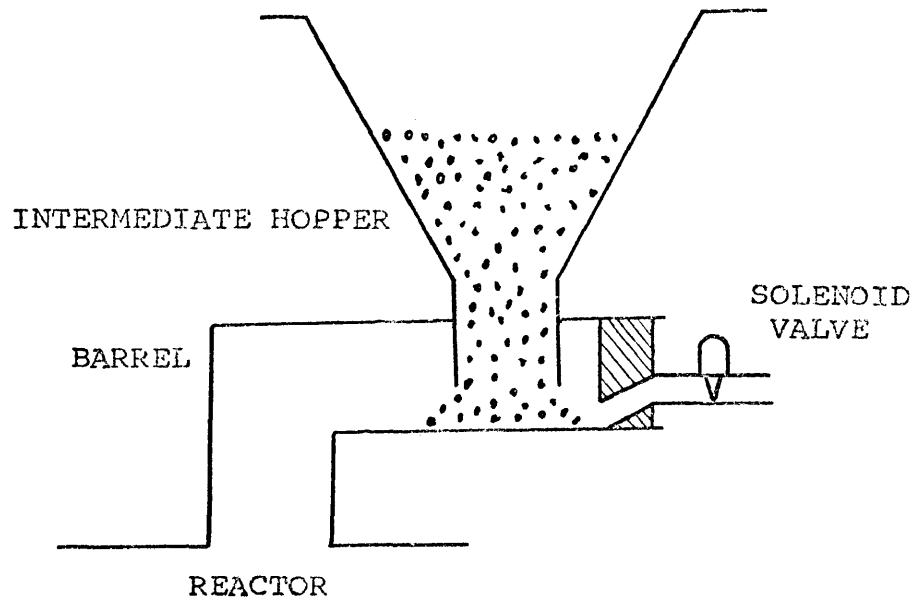
These five stages are mounted in a 5-in.-ID steel tube. The steel tube has a  $\frac{1}{4}$ -in. groove milled in its bottom extending between the centers of the end stages. The assembly is mounted in high-speed roller-bearings pressed into steel end-plates. The shaft is turned

at 5600 rpm by a 3-hp 3-phase electric motor. An oil cyclone, similar in design to the spent-shale cyclone, is attached to the demister outlet.

**FURNACE:** The furnace is a direct-fired propane unit. The air enters tangentially with a 10-degree forward tilt; the propane enters axially directly behind the air entrance. The furnace is constructed from a 44-in.-long schedule-40 two-in. pipe. The outlet of the furnace serves as the nozzle in the reactor by reducing the 2-in. pipe to whatever nozzle diameter and length desired. The furnace was insulated with  $\frac{1}{4}$  in. of asbestos tape and then covered with aluminum foil to reduce radiation losses. The furnace was started with an acetylene torch through a  $\frac{1}{4}$ -in. port in the furnace wall.

**GAS COMPRESSOR:** The gas compressor used was a Gast (Model 3040) operated at 800 rpm. The pump was driven by a 2-hp 3-phase electric motor. The pump has a 20-cfm capacity at 0-psi differential and 16 cfm at 10-psi differential. By changing the pulley sizes for 1060 rpm operation, the pump would have a 24-cfm capacity at 0-psi differential and 20 cfm at 10-psi differential. The pump body and rotor were constructed from carbon steel, and the vanes were carbon.

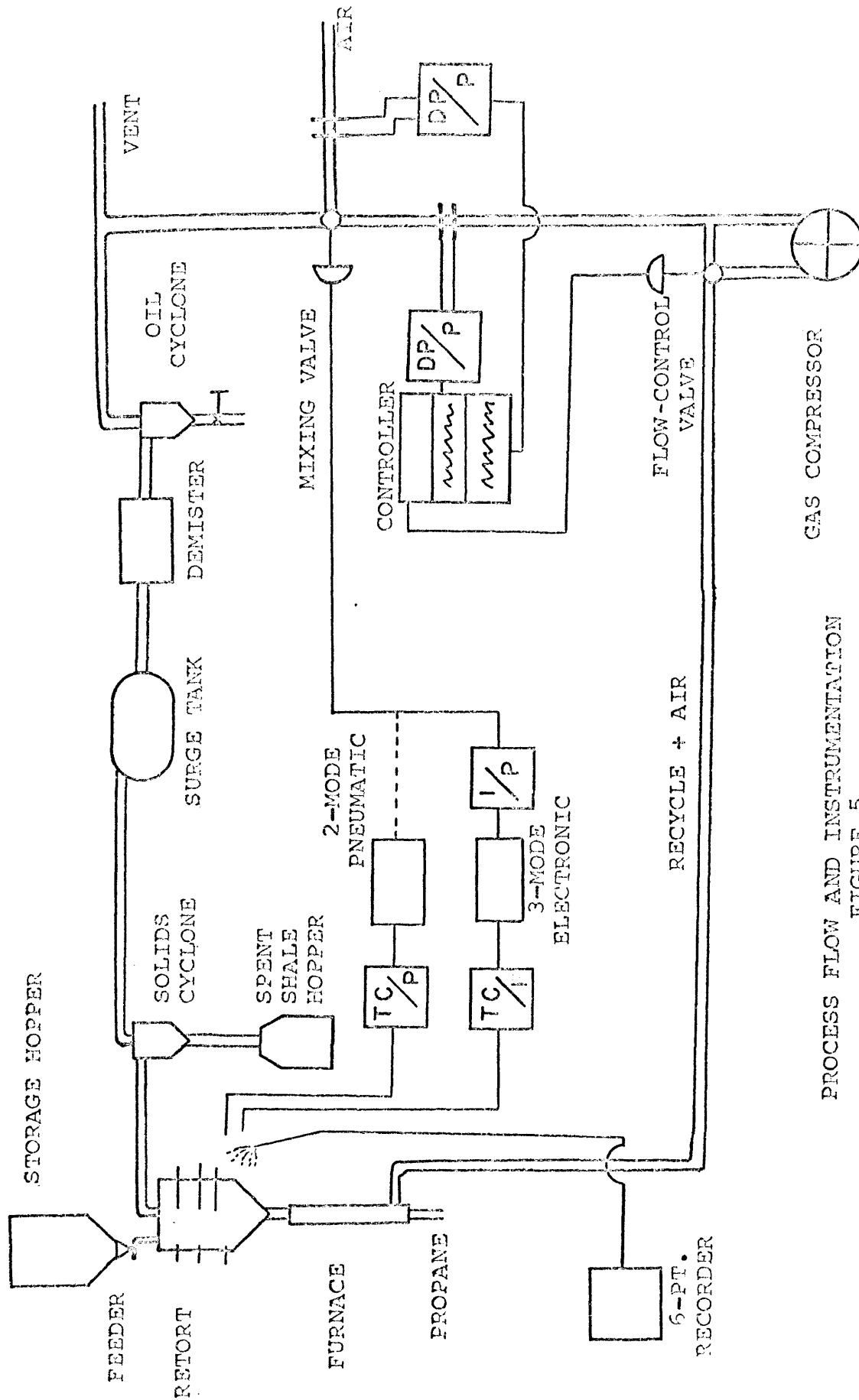
**FEEDER:** The horizontal barrel of the feeder is a 1-in.-square brass tube 4 in. long (Figure 4). A block inserted into the rear of the barrel has a 1/8-in.-high orifice the width of the barrel



FEEDER OPERATION  
FIGURE 4

and was used to provide uniform gas velocities across the barrel. An intermediate brass hopper is fitted into the feeder barrel and connected to an air-tight feed-storage hopper with a capacity of 106 lb of raw shale. The intermediate hopper is 4 in. square at the connection to the storage hopper and tapers to a 0.95-in. square neck. The neck extends into the barrel  $5/8$  in. leaving a  $3/8$ -in. clearance between the bottom of the neck and the bottom of the barrel.

FEED CONTROL: Because the feed rate is controlled by the pulsation rate of the feeder, an accurate electronic controller was designed and built for this purpose. The controller, fully adjustable from 13 to 250 pulses per min, contains provisions for two preset rates within these limits; it can also be controlled externally by means of an electronic resistance controller to any point within this range.



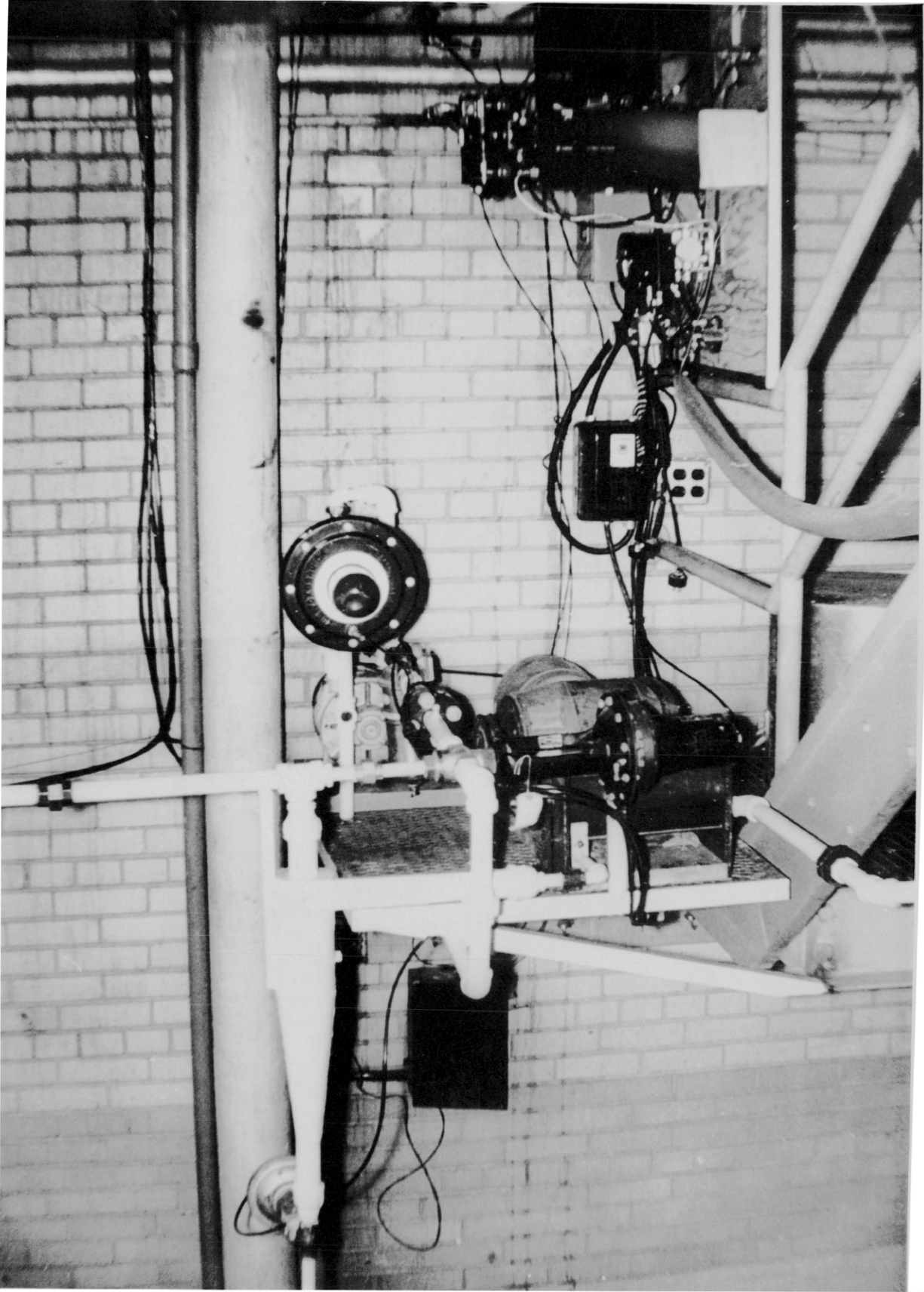
PROCESS FLOW AND INSTRUMENTATION  
FIGURE 5

INSTRUMENTATION AND CONTROL EQUIPMENT

For better process control and variable measurements, the process was highly instrumented. A combination of pneumatic and electronic controls and recorders were used to measure and control the total gas flow, air flow, and reactor temperatures.

**GAS FLOW:** Total gas flow, supplied from the Gast compressor as a mixture of air and recycle gas, was measured by an orifice plate with vena-contracta pipe taps. The pipe taps were connected to a Barton pneumatic indicating differential pressure-to-pressure transmitter (Model 225-601). The output was connected to a Moore (N/P Nullimatic) two-pen recorder and indicator, used in conjunction with a Moore (Model 50 M) two-mode controller. The controller output controlled the three-way bypass valve at the compressor, which controlled the amount of air bypassed to the compressor inlet and thereby controlled the total gas flow to the reactor. The flow was recorded by the recorder on a 0-to-100 basis.

**AIR FLOW:** Air flow was measured by an orifice plate 1 ft from the air inlet with vena-contracta pipe taps which were connected to a Foxboro pneumatic differential pressure to pressure transmitter





(Model 307887). The output was connected to the recorder used for total gas flow and recorded on the remaining pen. This flow was also recorded on a 0-to-100 basis.

TEMPERATURE MEASUREMENT: All the reactor temperatures were measured by 1/8-in.-OD, 6-in.-in-length, ISA-K calibration miniature thermocouples manufactured by the Thermo-Electric Company (Type No. 5K0120L). The thermocouples were connected to a Foxboro Dynalog (Model 933A) six-point recorder. The recorder was modified for ISA-K thermocouples and a 800- to 1800-°F range. Recycle- and vent-gas temperatures were measured by 1/4-in. industrial-type thermocouples in conjunction with a Thermo-Electric (Model 80237) portable potentiometer.

REACTOR-TEMPERATURE CONTROL: Two independent systems were available for controlling the reactor temperature. Both systems used the miniature thermocouple previously described for temperature measurement and a three-way mixing valve for controlling air rates.

The electrical system converted the thermocouple output to a 4- to 20-milliamp signal by means of a Transmation, Inc. (Model 310-K) convertor. This signal was fed into a Yamatake-Honeywell (Model NBC03-X-4) three-mode controller. The controller output was then transmitted to a Honeywell current to a pneumatic converter which controlled the mixing valve.

The pneumatic system converted the thermocouple output to a pneumatic signal by means of a Moore (Model 80237) thermocouple-to-

pneumatic converter and transducer. The output was then fed to a Moore (Model 50M) two-mode controller (Proportional plus reset) connected to a Moore (N/P Nullimatic) indicating remote station. The output of the controller was used to control the mixing valve.

## EQUIPMENT OPERATION AND DESIGN CRITERIA

Most of the equipment was specifically designed to handle a particular problem encountered in the operation of the unit. This included the basic reactor design, feeder, cyclone, surge tank, demister, and the control-and-measurement equipment.

REACTOR: The reactor consists of a conical transition section and a cylindrical section attached to the top of the transition section (Figure 3). In most of the previous works on spouted bed (13) the conical section was small in length compared with the cylindrical section. This design was altered for use as a spouted-bed oil shale retort in order to accommodate the highly exothermic combustion reaction. The combustion caused sudden increases in temperature and therefore would cause large velocity gradients along the axis of a cylindrical retort. The main body of the retort was made conical to increase the cross-sectional area of the retort as the volume of the gas increases. Without this change in area, the increase of gas velocities in the annulus fluidizes the upper part of the bed, destroying the spout, or entrains a large amount of shale, causing too rapid a carry-over rate. The use of the

conical reactor was also beneficial in that the nozzle-diameter to reactor-diameter ratio could be changed, without physically changing the reactor, by raising or lowering the nozzle outlet inside the reactor. Although this ratio could be changed by using different-size nozzles, the nozzle sizes were limited to approximately 0.5 in. Smaller sizes created pressure drops too large for stable furnace operation; larger sizes decrease the gas velocity in the nozzle to a point where poor spouting was obtained.

Contrary to the countercurrent flow pattern used in previous applications of spouted beds (13), the reacted solids are removed with the gas stream, with separation occurring beyond the reactor, giving co-current flow. The carry over is enhanced by using a conical exit tube located in the top of the reactor. The solids flow pattern in the reactor can be described as follows: as the spout rises above the main level in the reactor, most of the solids fall back into the annulus of the bed; however, some particles attain enough kinetic energy to rise far enough above the bed to enter the exit tube.

This method of removing solids from the reactor is selective in the particles that are carried out. As expected, the less dense and the smaller particles are preferentially removed (14). This selectivity is beneficial to the operation of the retort because the retorted particles are smaller and less dense than the unretorted particles. The retorting operations that produce these changes are: 1) the solids become less dense from the loss of organic matter and

carbonate decomposition; 2) the shale becomes softer as it is retorted and undergoes attrition to produce fine particles.

If the feed rate exceeds the carry over, the side arm can be used as a solids overflow into a sealed hopper.

**FEEDER:** Because this is a steady-state process, shale must be fed into the reactor at a constant rate. The conventional types of solids feeders were unacceptable for use with the unit because of difficulties in scale-down. A small pulse feeder, developed specifically for this application, is operated as follows: fresh shale contained in the storage hopper is gravity fed into the intermediate hopper of the feeder unit as shown in Figure (4). The shale flows into the square barrel of the feeder until it reaches the natural angle of repose. A blast of air from the rear of the barrel forces all of the shale that extends below the neck of the intermediate hopper into the reactor. The blast of air is kept as short as possible to keep the air used to a minimum. Shale again flows into the barrel, and the steps are repeated. The flow rate of shale can be regulated by controlling the frequency of this cycle.

**CYCLONE:** The solids in the gas stream are removed by a cyclone attached to the reactor outlet. This 4-in. cyclone is capable of removing particles greater than 10 microns in diameter (15), which in most cases accounts for 90 percent of solids. The cyclone

also serves as an air heat exchanger for cooling the gas stream.

**SURGE TANK:** The surge tank performs three main functions: as a surge tank to reduce any pressure surges in the system and smooth out gas flow; as a heat exchanger in the same manner as does the solids cyclone; as a means of removing most of the remaining solids in the gas stream. Water-mist nozzles are placed in the tank for enhancing heat exchanger and solids removal. The water spray serves as a heat-transfer medium in that it is evaporated by the incoming hot gas and then is condensed on the tank walls or other water particles, thus many times increasing the effective heat transfer. The water also wets the solid particles, causing them to settle out more efficiently.

**DEMISTER:** The oil mist in the gas stream forms a very stable, submicron mist upon condensation. The high-speed impingement effect of the demister coagulates the mist particles on the demister stages, and the oil drops are then thrown against the demister wall forming a liquid seal between the demister stages. The oil flows along the walls and is pumped through the stages to the oil cyclone at the demister outlet. The oil is then collected in a small reservoir at the bottom of the cyclone.

**GAS FLOW:** The suction side of the gas compressor is connected

to the common port of the three-way mixing valve (see temperature control) and to another three-way valve used to control flow rate. The compressor outlet is connected to the common port of the three-way flow-control valve with the third port of this valve going to the reactor via the furnace. This construction enables the flow to be controlled by regulating the bypass rather than throttling the suction or discharge side of the valve. This provides smoother flow control and keeps a constant load on the compressor. The total gas flow is measured by an orifice plate between the two three-way valves. This location was chosen over measurement on the discharge side because the suction pressure remained relatively constant where the discharge pressure was affected by all the pressure drops in the system. Vena-contracta pipe taps are used to give maximum-measure pressure drop with the minimum unrecoverable pressure loss. Although a single-mode controller would have been sufficient for gas-flow control, a two-mode controller was used.

TEMPERATURE CONTROL: The temperature is controlled by the amount of oxygen put into the reactor, thereby limiting the amount of burning of the organic products from the retorting operation. The gas stream from the oil cyclone, being essentially inert, is mixed with fresh air thus adjusting the amount of air fed into the reactor. The three-way mixing valve is controlled to give the correct recycle-to-air ratio for correct temperature control. Both locations

one and two (see Figure 3) was used for temperature control. Location two provided the closer control; location one provided a smoother control because of the thermal capacitance and damping of the outlet. Miniature thermocouples were used in the reactor for their fast response to temperature changes and because they gave smaller disturbances to solids and air flow in the reactor. Although the two independent control systems were installed, the electronic system was used exclusively after its installation. The pneumatic system was used as a continuous monitor because the six-point recorder had a 40-sec cycle time. The three-mode electronic controller was used in preference to the two-mode pneumatic because of the availability of the rate mode and a larger proportional band. The rate mode was very useful to counteract the dead time lag of the system. The two systems can be used in conjunction with each other for cascade control. This use can be accomplished by converting the pneumatic output to a current signal and using it as a set-point input to the electronic controller.



EXPERIMENTAL PROCEDURE

The retort must be operated at temperatures above the flammability limit of the organic product; therefore, the retort must be preheated by the furnace to reach this temperature.

The preheat and start up of the reactor were performed as follows: The control air and feed air were turned on, and the electrical controls and recorders were plugged into electrical outlets. The demister and compressor motors were then turned on. The gas flow into the furnace was allowed to stabilize before the furnace was started. While the furnace was in operation, the temperature controller was turned to manual control with zero output so that no recycle could be returned to the furnace. The propane feed rate was adjusted to give maximum furnace temperature. When the reactor reached about 1000 °F, the shale feeder was turned on and adjusted to the desired output. When the retort outlet temperature reached 1200 °F, the propane feed was slowly decreased until the excess air started to ignite the oil; upon this ignition, the temperature in the retort started to rise more rapidly. The propane was then shut off and the temperature controller set to automatic control at the desired set point.

Because the gas flows and reactor temperatures were automatically controlled and recorded, the operation after startup was greatly simplified. If it was necessary to use the overflow tube, the valve opening the overflow had to be opened every one-half hour and the weight of the removed shale determined. Samples of oil were collected, weighed, and labeled for further analysis. Samples of the vent gas were taken for immediate chromatographic analysis. Samples were taken in pairs because they were analyzed with two columns and because the sample bottles contained only enough gas for one analysis. A molecular sieve column was used to determine carbon monoxide, methane, oxygen, and nitrogen content. A silica-gel column was used to separate the larger hydrocarbons from each other and from the oxygen-nitrogen mixture.

The shutdown procedure is the reverse of the startup procedure up to the point where the furnace is started. In addition, the storage hopper is refilled to determine the amount of shale used during the run. The spent-shale hopper is weighed in order to determine the amount of spent shale and then emptied for use in the next run.

Preventive maintenance also had to be performed on some of the equipment. The surge tank had to be removed and cleaned after every 6 hours of retorting. The line connecting the surge tank and demister had to be cleaned after each run to insure no plugging problems. The compressor had to be washed with organic solvent to remove the oil mist so as to prevent sticking of the carbon vanes in the rotor.

### DISCUSSION OF RESULTS

The good agreement of the calculated results with the experimental results indicates that the mathematical model accurately described the system within the range of the data points. The average error between the calculated percent-air and the experimental percent-air was 2 percent, whereas the estimated error in measurement of the percent air was 4 percent. The experimental error was due mostly to estimating the average air flow from the strip-chart recorder.

The large errors in runs 2 and 12 were characterized by large temperature gradients in the reactor and unstable temperature control. This condition indicates that the solids were not circulating in the reactor because of complete collapse of spout or loss of spout shape (1).

The reproducibility of the data can be seen between runs 11 and 16. Although the runs are not identical, the parameters are close enough for comparison, as shown by the 1-percent difference in calculated air rates. The differences in the experimental air rates is 2 percent, well within experimental error.

The range of variables reported in the data is the limits in which the retort was operational. Runs attempted outside these

limits were failures. Temperatures had to be kept below 1200 °F so that the gas temperatures in the demister were below 300 °F, preventing bearing failure. Temperatures below 950 °F produced unstable control of the system with temperature oscillations below the flammability limit of the organic, causing flame out. At retort temperatures below 1150 °F, the maximum feed rate was 15 lb per hr; higher rates caused the reactor to fill because the carry-over was insufficient. At 1200 °F the gas velocities and a higher attrition rate were sufficient to maintain a carry-over rate of approximately 20 lb per hr.

The calculated results in Tables 2 and 3 are for conditions in run 6 with the parameter indicated being varied. Table 2 shows the effect of preheating the gas stream to 1200 °F. Without preheat the oil yield was 32 percent, indicating a possible doubling of the yield with increase in inlet gas temperature to 1200 °F. Table 3 shows the effect of increasing the shale-feed rate. Even if a rate increase to 32 lb per hr were possible, the oil yield would be only 58 percent. The main reason for the poor oil yields, even with preheat or increased feed rate, is the large heat loss compared with the other heat requirements (approximately 20 percent). The portion of the heat loss would be substantially reduced in a larger size unit, improving the oil yield.

Atmospheric distillation (Table 4) of samples of oil products indicates the lack of low boiling components, substantiating the

TABLE 2 (Preheat effects--Run 6)

T-gas	% Oil Yield *
65 °F	32
400	41
500	44
600	47
700	49
800	51
900	53
1000	56
1100	59
1200	62

TABLE 3 (Feed effects--Run 6)

Feed Rate lb/hr	% Oil Yield *
10	17
12	26
14	33
16	38
18	42
20	46
22	48
24	50
26	52
28	54
30	56
32	58

\* Theoretical Oil Yield (see theory)

assumption that the light components were burned in the retort. The samples used were from runs 9 and 16, which are the extremes in operating temperatures; both show similar properties. The water was 20 percent; cracking of the oil was started at the 50-percent point.

Solids content of the oils varied between 25 and 45 percent, indicating an inefficiency of solids removal.

TABLE 4

## Run 16 - Atmospheric distillation

Percent	°F
0	---
10	202
20	202
30	360
40	490
50	552
cracking started	

Percent solids in initial sample-48.8 %

## Run 9 - Atmospheric distillation

Percent	°F
0	---
10	200
20	204
30	340
40	475
50	515
cracking started	

Percent solids in initial sample-45.2 %

### CONCLUSIONS AND RECOMMENDATIONS

The results obtained from the research on the operating criterion of a spouted-bed oil shale retort are as follows:

1. The operational limits of the present retort are 950 to 1200 °F with shale rates of 10 to 20 lb per hr.
2. The heat required by the process is supplied by the combustion of the light hydrocarbons as they are produced from the raw shale.
3. The combustion in the retort is a complete combustion to carbon dioxide with approximately stoichiometric quantities of oxygen.
4. The heat-and-mass balances using data obtained from the literature cited and experimental data gave a good mathematical representation of the process.
5. Flow rates could be substantially increased to give a residence time of between 5 and 10 minutes, while still producing complete pyrolysis.
6. Under circumstances of high temperature and an oxidizing atmosphere, the fine particles of spent shale can be explosive.



From the operation of the unit and analysis of the results obtained, recommendations can be made in two areas--equipment design for the spouted-bed retort or similar type entrained particle retorts and application of further study of the techniques used in this thesis.

The following recommendations are made for further design of the retort and support equipment:

1. The demister be designed with a manifold for draining the oil from each stage.
2. The bearings in the demister be fitted with smothering glands to increase bearing life.
3. The connection between the mixing valve and the reactor be kept as short as possible to decrease dead time lag.
4. A more efficient solids removal system be used in place of the single cyclone.

Further studies could be made in the following areas:

1. A study of reactor designs be made to optimize the gas flow needed for spouting.
2. The possibility of preheating from spent shale combustion be investigated to produce anaerobic retorting at lower temperatures.
3. A more sophisticated system be used to test the theoretical model.

## Appendix 1 - Data

A typical set of recorder outputs is shown at the end of the data (Row 10). The circular chart is from the Foxboro six-point recorder; time indicated on the chart is three times real time due to an 8-hr clock being used in place of a 24-hr clock. The strip chart indicated the total gas flow (the straight line at 15) and the air rate (the oscillating line). These values can be converted to flow rates by use of orifice-calibration curves.

Units and nomenclature for data:

T - Temperature at reactor outlet ( $^{\circ}\text{F}$ )

V - Volume of reactor (lb)

Feed - Feed rate (lb/hr)

Spent - Spent-shale rate (lb/hr)

Gas - Total gas flow into reactor (cu ft/min)

Air - Fresh air into reactor (cu ft/min)

Run 1  
T = 1080  
V = 8.5  
Feed = 21  
Spent = 17.2  
Gas = 9.2  
Air = 4.0

Run 2  
T = 1180  
V = 2.5  
Feed = 15.2  
Spent = 9  
Gas = 9.2  
Air = 4.3

Run 4  
T = 1070  
V = 7.0  
Feed = 12.3  
Spent = 10.0  
Gas = 7.60  
Air = 2.7

Run 6  
T = 1100  
V = 9.0  
Feed = 14.0  
Spent = 10.8  
Gas = 8.0  
Air = 3.1

Run 7  
T = 1050  
V = 5.0  
Feed = 13.5  
Spent = ---  
Gas = 5.5  
Air = 2.2

Run 8  
T = 1200  
V = 7.5  
Feed = 19.3  
Spent = ---  
Gas = 7.3  
Air = 3.6

Run 9  
T = 1200  
V = 7.0  
Feed = 10.6  
Spent = 9.8  
Gas = 7.0  
Air = 2.8

Run 10  
T = 1020  
V = 5.0  
Feed = 9.5  
Spent = 7.3  
Gas = 7.0  
Air = 2.2

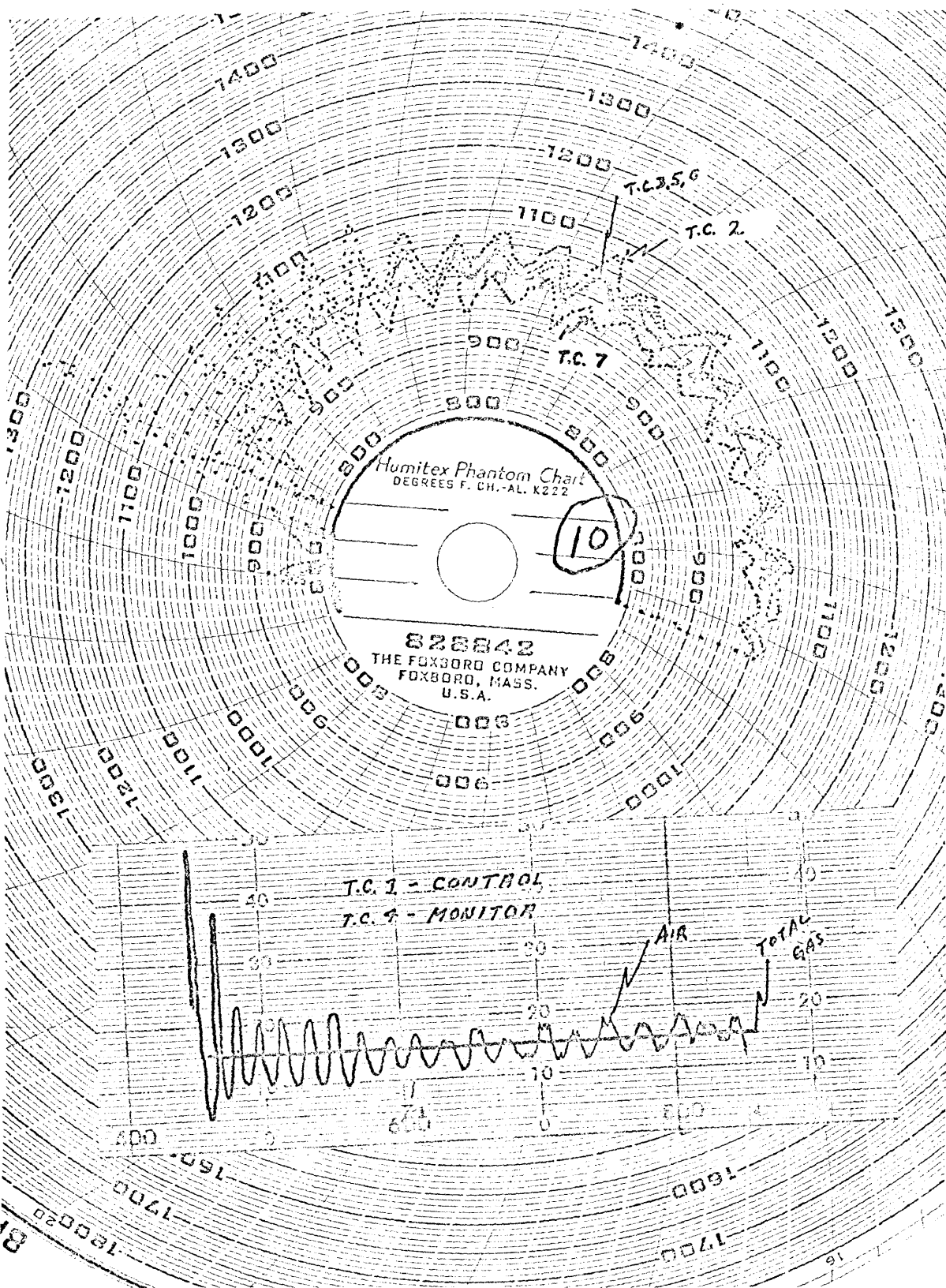
Run 11  
T = 1000  
V = 4.5  
Feed = 10.0  
Spent = ---  
Gas = 7.5  
Air = 2.5

Run 12  
T = 1050  
V = 2.5  
Feed = 14.1  
Spent = 10.0  
Gas = 7.0  
Air = 2.2

Run 14  
T = 1075  
V = 9.5  
Feed = 13.2  
Spent = 8.5  
Gas = 8.2  
Air = 2.9

Run 15  
T = 1180  
V = 2.0  
Feed = 12.3  
Spent = 6.5  
Gas = 7.4  
Air = 2.6

Run 16  
T = 990  
V = 4.3  
Feed = 10.4  
Spent = 8.4  
Gas = 7.6  
Air = 2.3



Run 10-- Circular chart (Foxboro Dynalog) and Strip Chart

## Appendix 2 - Oil Shale Analysis

Total carbon - 13.19 wt. percent

Total hydrogen - 1.31 wt. percent

Total ash - 72.02 wt. percent

Heat content based on raw-shale weight (30 to 500<sup>0</sup>C)

Spent shale - 191 Btu/lb (based on spent shale weight)

Spent shale - 168 Btu/lb (based on raw shale weight)

Raw-shale retorting - 46 Btu/lb (based on raw shale weight)

Weight loss - 12 percent

## APPENDIX 3

The following is a direct computer output for the data  
in Appendix 1 using the digital program listed in Appendix 4.

RUN 16.00

T-gas 65.00 F

T-solids 60.00 F

FEED 10.40 lbs/hr

REACTOR TEMP. 995.00 F

AVG. RES. TIME 188.02 min.

GAS 7.60 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
27.56	9.27	32.09	31.00	3.40

RUN 15.00

T-gas 65.00 F

T-solids 60.00 F

FEED 12.30 lbs/hr

REACTOR TEMP. 1180.00 F

AVG. RES. TIME 74.83 min.

GAS 7.40 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
22.80	10.97	41.54	42.00	1.10

RUN 14.00

T-gas 65.00 F

T-solids 60.00 F

FEED 13.20 lbs/hr

REACTOR TEMP. 1075.00 F

AVG. RES. TIME 33.10 min.

GAS 8.25 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
32.03	11.77	35.20	35.00	.59

RUN 12.00

T-gas 65.00 F

T-solids 60.00 F

FEED 34.10 lbs/hr

REACTOR TEMP. 1050.00 F

AVG. RES. TIME 163.15 min.

GAS 7.00 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
----------------	-------------	------------	-----------	---------

40.99	12.57	38.48	32.00	16.83
-------	-------	-------	-------	-------

RUN 11.00

T-gas 65.00 F

T-solids 60.00 F

FEED 10.00 lbs/hr

REACTOR TEMP. 1000.00 F

AVG. RES. TIME 206.98 min.

GAS 7.44 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
----------------	-------------	------------	-----------	---------

25.67	8.92	32.30	33.00	2.15
-------	------	-------	-------	------

RUN 10.00

T-gas 65.00 F

T-solids 60.00 F

FEED 9.50 lbs/hr

REACTOR TEMP. 1020.00 F

AVG. RES. TIME 242.15 min.

GAS 7.00 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
----------------	-------------	------------	-----------	---------

23.39	8.47	33.65	31.00	7.89
-------	------	-------	-------	------

RUN 9.00

T-gas 65.00 F

T-solids 60.00 F

FEED 10.60 lbs/hr

REACTOR TEMP. 1200.00 F

AVG. RES. TIME 260.39 min.

GAS 7.00 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
----------------	-------------	------------	-----------	---------

8.49	9.45	44.86	40.00	10.83
------	------	-------	-------	-------

RUN 8.00

T-gas 65.00 F

T-solids 60.00 F

FEED 19.30 lbs/hr

REACTOR TEMP. 1200.00 F

AVG. RES. TIME 178.77 min.

GAS 7.30 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
36.85	17.21	54.05	49.00	9.34

RUN 7.00

T-gas 65.00 F

T-solids 60.00 F

FEED 13.50 lbs/hr

REACTOR TEMP. 1050.00 F

AVG. RES. TIME 170.39 min.

GAS 5.50 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
44.89	12.04	43.78	40.00	8.64

RUN 6.00

T-gas 65.00 F

T-solids 60.00 F

FEED 14.00 lbs/hr

REACTOR TEMP. 1100.00 F

AVG. RES. TIME 295.72 min.

GAS 8.00 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
32.17	12.48	38.43	38.00	1.11

RUN 4.00

T-gas 65.00 F

T-solids 60.00 F

FEED 12.30 lbs/hr

REACTOR TEMP. 1070.00 F

AVG. RES. TIME 261.80 min.

GAS 7.60 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
30.56	10.97	36.38	35.00	3.79



RUN 2.00

T-gas 65.00 F

T-solids 60.00 F

FEED 15.20 lbs/hr

REACTOR TEMP. 1180.00 F

AVG. RES. TIME 75.68 min.

GAS 9.20 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
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25.88	13.55	39.65	47.00	18.53
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RUN 1.00

T-gas 65.00 F

T-solids 60.00 F

FEED 21.00 lbs/hr

REACTOR TEMP. 1080.00 F

AVG. RES. TIME 186.20 min.

GAS 9.20 cfm

OIL YIELD-wt %	SPENT SHALE	CALC AIR-%	EXP AIR-%	% ERROR
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46.94	18.73	39.21	44.00	12.21
-------	-------	-------	-------	-------

## APPENDIX 4

This program of the mathematical model was written for use on a LGP-30 digital computer manufactured by Royal Precision. The language used is in the 24.2 system.

```
;0004000°/0004000°
xf6300°xu0400°xi0000°xz0000°
10900°u0600°b0900°a0800°
h0900°b0902°a0800°h0902°
b0905°a0800°h0905°xz0000°
xz0000°xz0000°b0804°a0905°
a0805°xh0010°xy0000°u0962°
xh0000°zy0000°a0812°u0814°
d0818°u0904°h0960°xz0000°
```

```
b0805°a0905°a0810°xh0010°
xy0000°u0962°xh0000°xy0000°
a0812°u0816°d0820°u0904°
h0958°a0960°h0956°u0822°
h0954°b0906°u0906°h0952°
a0826°h0948°b0900°u0900°
xy0000°a0952°u0828°h0946°
b0905°a0900°u0832°a0946°
```

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xz0000°u0838°h0942°b0902°
u0836°a0942°a0834°u0914°
u0802°a0840°h0940°b0952°
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```

bu

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 m0802°a0840°x00000°h0928°  
 b0918°a0956°h0916°b0904°  
 m0856°a0858°a0920°h0922°  
 b0952°m0846°h0938°b0905°  
 m0844°a0842°a0938°m0916°  
 h0926°b0952°m0852°h0934°

b0906°m0850°a0848°a0934°  
 m0922°h0924°b0954°a0914°  
 a0924°a0926°a0928°s0940°  
 a0714°a0700°h0762°m0702°  
 h0918°b0762°m0704°h0920°  
 b0762°m0706°h0760°b0914°  
 m0802°a0840°h0758°b0760°  
 a0862°a0758°m0860°h0756°

s0912°x00000°a0756°m0860°  
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 s0708°t0300°b0762°h0716°  
 u0114°  
 .0000000°

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 b0912°x00000°x00002°x00000°  
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 10.jzj00°

b0906°xz0002°xu0000°,0000007°  
 zj101010°  
 20r340ak°vjs810.j°zj20r4ek°ek10.jzj°  
 20r414ek°ekzj1000°b0909°d0904°m0800°h0962°  
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 4020g8ek°ekzj1000°b0914°xz0002°  
 u0300°  
 .0000000°

;0004500°/0004000°  
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 zjck4r0ak°h0200j4h°18zjy4h4°ek418ak410°  
 -j4r8ek4zj°205860ak°p4ek4ek4°zj4ek4ek4°  
 18ek460ek°ek418ek420°20zj4ek4h4°r410-j20°  
 5860ek4zj°p4ek4ek4h4°r410-j20°586058zj°  
 ek4r4r40j°r4104000°u0006°  
 .0004000°

4800°460°+00°+60°+00°+19986°-00°+906°+02°-°21892°-00+°  
 1090°+02°-°1°+00°+170°+03°-°280°+03°-°  
 100°+00°+124°+00°+57000°+00°+31°+06°-°242°+03°+°  
 56°+06°-°492°+00°+172°+03°-°3263°-00°+647°+02°-°  
 3559°+07°-°505°+00°+3614°-00°+580°+02°-°3361°+06°-°  
 3826°-00°+763°+02°-°2154°+07°-°71°+02°-°1°+02°-°18°+00+°  
 100°+00°+29°+02°-°g°

4700°16500°+00°+73°+03°-°6°+02°-°95°+03°-°1°+02°-°  
 108°+03°-°892°+03°-°3500°+00+°°°f°

Data call sequence: T-solids, T-gas, Feed Rate, Reactor Temperature,  
 Volume, Run Number, Exp. % Air, and Gas Rate.

Appendix 5  
Additional Equations And  
Relationships for Theoretical Model

The following equations were obtained from data given in Himmelblau (11).

$$\text{For } N_2 \text{ and } O_2 \quad H = -3263 + 6.47 T + 3559 \times 10^{-7} T^2$$

$$CO_2 \quad H = -3614 + 5.80 T + 3361 \times 10^{-6} T^2$$

$$H_2O \quad H = -3826 + 7.63 T + 2154 \times 10^{-7} T^2$$

where:  $T$  (=)  $^{\circ}R$  and  $H$  = enthalpy (=) Btu/lb mole

The following equations, for calculating rate constants for the thermal decomposition of the mineral carbonates, were obtained from Jukkola (4):

$$\text{For } CaCO_3 \quad \log k = 9.06 - 19986/T$$

$$(MgCa) CO_3 \quad \log k = 1.90 - 21843/T$$

where:  $k$  (=) 1/min and  $T$  (=)  $^{\circ}R$

From Table 1:

initial concentration of  $CaCO_3$  = 0.17 lb/lb shale

$(MgCa)CO_3$  = 0.28 lb/lb shale

The following relationships are calculated on the basis of 1 lb of raw shale.

$$0.17 \text{ lb CaCO}_3 = 0.02 \text{ lb carbon}$$

$$0.28 \text{ lb (MgCa) CO}_3 = 0.027 \text{ lb carbon}$$

$$\text{Total} = 0.0470 \text{ lb carbon}$$

Analysis of raw shale gave: 0.1317 lb of total carbon & 0.0131 lb of hydrogen

$$\text{Organic carbon} = 0.1317 - 0.0470 = 0.0947 \text{ lb}$$

$$\text{Total organic content} = 0.0947 + 0.0131 = 0.1078 \text{ lb}$$

$$10.78 \% \text{ organic content} = 10 \text{ gal/ton Fischer assay}$$

The following are on the basis of 1 lb organic.

0.0733 lb-moles carbon and 0.06 lb-moles hydrogen

therefore:



Formed: 0.0733 lb-moles  $\text{CO}_2$   
0.0600 lb-moles  $\text{H}_2\text{O}$

Used 0.1033 lb-moles  $\text{O}_2$   
or  
0.493 lb-moles air

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