1 of 1

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HIGH EFFICIENCY SHALE OIL RECOVERY

FINAL REPORT

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ENERGY RECOVERY TECHNOLOGY

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PROJECT SUMMARY

The Adams Counter-current shale oil recovery process is an improved retorting technology enabling highly efficient oil recovery from oil shale. The high efficiency results primarily from the following facts: it (1) recovers the ash heat to preheat the feed ore, (2) burns and uses the coke energy and (3) operates without using hot ash recycling as a heat carrier. This latter feature is doubly important, contributing to high oil yield and to the generation of highly reactive coke which can be burned below 1000°F, avoiding the endothermal calcination of the mineral carbonates and helping to clean the ash of contaminants. This project demonstrates that oil shale can be retorted under the specified conditions and achieve the objectives of very high efficiency.

The project accomplished the following: (1) 51 quartz sand rotary kiln runs provided significant engineering data. A heat transfer value of 107 Btu/hr/ft²/°F was obtained at optimum RPM. The data are compared with the literature. (2) Eight oil shale samples were obtained and preliminary shakedown runs were made. Five of the samples, those with prior analytical data, were selected for kiln processing and twelve pyrolysis runs were made on the five different oil shales. All of the runs exhibited a complete absence of any surface-adhering solids or particle agglomeration. The average heat transfer in the rotary kiln was 78 Btu/hr/ft²/°F for Green River oil shale, which will provide adequate heat exchange for the success of the Adams kiln. (3) Average oil recovery was 109% of Fisher Assay. (4) Retorted residue from all five samples was oxidized at approximately 1000°F. The ash from these runs was oxidized to varying extents, depending on the oil shale type and oxidizing temperatures. While 1000°F is adequately hot to provide process heat from coke combustion for these ores, some Eastern oil shales, without mineral carbonates, may be oxidized at higher temperatures, perhaps 100-300 degrees hotter, to obtain a more complete oxidation and utilization of the coke.

INTRODUCTION

Background: The Counter-current Heat Exchange between Solid Streams or CHESS¹ oil recovery process was the subject of two SBIR Phase I projects prior to the current project. In 1987 the small batch rotary kiln was constructed and the project demonstrated fairly efficient recovery of tar sand bitumen. In a 1990 project, an important feature of the CHESS retort, the gas lock, was demonstrated, showing that the lock could effectively conduct granular solids from the pyrolyzer to the combustor while disallowing passage of either the pyrolysis or the combustion gases.²

The CHESS process is an inexpensive, high efficiency oil and heat recovery kiln for retorting oil shale and other fossil bitumens with minimal environmental impact. It consists of a rotary kiln with an inner concentric high surface area cylinder. The cold ore feeds into the inner cylinder and heats as it passes the hot burning ash, moving in the opposite direction in the annular space of the outer cylinder. Thus it achieves high heat recovery without mixing the solid streams.³

Project Objective: The overall project objective is to demonstrate the high efficiency of the Adams CHESS process. The efficiency is first being demonstrated on a small scale, in the current phase, after which the demonstration will be extended to the operation of a small pilot plant. Thus the immediate project objective is to obtain data on oil shale retorting

operations in a small **batch** rotary kiln that is representative of operations in the proposed **continuous** process pilot plant. Although an oil shale batch sample is sealed in the batch kiln from the start until the end of the run, the process conditions for the batch are the same as the conditions that an element of oil shale would encounter in a continuous process kiln. Similar chemical and physical conditions (heating, mixing, pyrolysis, oxidation) exist in both systems.

Important data objectives for this phase of the project were demonstrated: (1) that the heat recovery forecast for this project is reasonable, (2) that the Adams concept oil shale kiln would run continuously and not plug up from particle agglomeration and adhesion to inner kiln surfaces, (3) that oil shale coke could be burned at temperatures as low as 1000°F (for the carbonate-containing Green River oil shale) to provide adequate process heat, even from lean ore. Other objectives were also demonstrated: (4) that the oil recovery would be substantially higher than recycled ash processes, which are typically below 90% of Fisher Assay, and (5) that low heat and temperature requirements equate to a minimal environmental impact.

Heat transfer for this project is high by standards of conventional rotary kilns. The reason is because (1) the heat transfer is not from a hot gas to the solids but from solids to solids, and (2) there is relatively high surface velocity between the wall and the solids. Heat transfer in the CHESS kiln should be compared, not to conventional kilns (of about 10 Btu/hr/ft²/°F), but to fluidized bed systems (about 100 Btu/hr/ft²/°F). Desai compared experiments with flowing granular media beds with fluidized beds and showed that heat transfer was generally higher for the flowing beds than for fluidized beds.⁴

EXPERIMENTAL

Equipment Description

Kiln: The batch kiln used in this project is a modification of the unit constructed in 1987. A description of the kiln is given in Figs. 1, 2 and 3, which show cross sections of the main features of the kiln. Fig. 1 is a cross section of the overall furnace and kiln assembly. Dimensions of the kiln are given in Fig. 2 and details of the reactor section are shown in Fig. 3. The rotational velocity (RPM) was controlled by a variable speed motor (not shown). Kiln RPM ranged from 0-200 RPM or a surface velocity of 0-280 ft/min. (The surface we are concerned with is the internal kiln wall where the granular particles slide and are heated or cooled as the kiln rotates. The kiln has an ID of 5.4", an internal circumference of 1.41 ft, so the surface velocity in ft/minute is just 1.41 X RPM).

Furnace and Temperature Control: The kiln furnace was designed originally with three heaters (see Fig. 3, HTR #1, #2 and #3) to provide a flat temperature profile (which was partially successful). However, temperature uniformity was greatly improved in this project with the addition of heaters #4 and #5 on the kiln ends. The temperature heat-up was controlled by a system installed for this project in an IBM compatible 286 process-automation computer. The computer interface to the kiln consisted of DAS-08, MUX-32 and CTR-05 boards from ComputerBoards Inc. Eighteen thermocouples were used. The output from 16 of these were fed into the MUX-32 multiplexer and then to the CIO-AD08 analog-to-digital converter board. The CTR-05 controlled the 240 volt, five-zone power and temperature control by means of time-proportioning output through five pairs (driver plus power controller) of solid state relays.

LEGEND: 1. STATIONARY CONNECTOR FOR GAS INLET
2. THERMOCOUPLE SLIP RING CONNECTIONS
3. HEATER POWER SLIP RING CONNECTIONS
4. ROLLER BEARING SUPPORTS FOR KILN
5. DRIVE PULLEY

6. THERMOCOUPLE LOCATIONS (+)
7. EXIT GAS FILTER

8. COOLING WATER INLET/OUTLET
9. COOLED GAS/VAPOR OUTLET
10. SLIP RING CONNECTIONS TO THERMOCOUPLE AND HEATER IN FILTER

⑥

BATCH KILN CROSS SECTION

ENERGY RECOVERY TECHNOLOGY - 1992

FIG. 1

FIG. 2: KILN DIMENSIONS

HEAT EXCHANGER LOCATIONS (■)

FIG. 3: CROSS SECTIONAL DETAIL OF REACTOR ZONE

Computer Program: Time proportioned temperature control was provided by means of our own software "Kilntrol" program. *Kilntrol* provided for complete PID control (Proportioning, Integral and Derivative parameter control) and allowed for the desired versatility and alterations as they were needed.

Sample Preparation

Quartz Sand: When a material of known heat capacity is heated in the rotary kiln, the Heat Transfer Coefficient (U) between the kiln and the material can be measured. Commercial quartz sand (30 and 70 mesh) was used as a standard granular material of known heat capacity to obtain the basic Heat Transfer characteristics of the kiln.

Oil Shale: Eight primary oil shale samples were collected from institutions as follows: Four samples from Western Research Institute (WRI), Laramie, WY; one sample from Lawrence Livermore National Laboratory (LLNL), Livermore, CA; and three samples from the University of Utah (U of U), Salt Lake City, UT. Typical values of Fisher Assay were included with the five samples from WRI and LLNL. Consequently, these five samples were chosen for project processing. The LLNL sample is referred to as *Occidental* and the WRI samples as *Parachute*, *Tipton*, *Kentucky* and *Indiana*. All are Green River samples except the latter two which are Eastern oil shales. These and one U of U sample were crushed to -7 mesh (i.e. passing through 7 mesh sieve). These primary samples (20 kg each) were then riffle-divided into secondary sample batches (1 kg each), and then sealed in an atmosphere of CO₂ to minimize any oxidation of the fine particles in case there should be any significant delay in the time of processing the different samples. Data that accompanied the WRI and LLNL samples are included in Appendix E. The values are approximate to our samples, as can be seen by the wide spread in some of the data.

Assembly and Operation

Kiln: The furnace is formed of top and bottom halves, with the two halves hinged together in the back. The top is lifted and rotated toward the back side of the stand for access to the kiln. The end closure, inlet tube, drive pulley, "insulator can" (in the kiln center with #4 heater), the auger blades and internal thermocouples are all inserted and removed as a single assembly unit when closing and opening the kiln. Thus sand or oil shale was loaded into the cylindrical kiln, with the gas filter, item 7, already in place. (Item numbers refer to numbers in Fig.1.) Then the end closure with auger blades etc. is assembled with the closure O-ring sealing the solids inside. The kiln is next placed in the furnace/stand cradle where the three slip rings (items 2, 3 and 10) mate with the slip ring brushes attached to the stand (brushes not shown), and all the electrical and instrumental connections to the rotary kiln are then complete. A pulley belt in position over the motor and drive pulleys (item 5) is taut as the assembly is tightened into place by means of two clamps, one over each roller bearing (items 4). After making the gas line and water connections, the run is ready to begin.

Sand Runs: Quartz sand is essentially inert for our application, below 1000°F. Nevertheless, nitrogen sweep gas flow was used with the sand runs to simulate the conditions of oil shale runs. Gas entered the kiln at room temperature and exited at kiln temperature. Cooling water was used in the Exit Tube condenser to protect the O-ring seals on the rotary outlet seal. Thereafter the gas was vented directly without other treatment.

Oil Shale Runs: Nitrogen sweep-gas flowed through the kiln at 14 liters/min (space

velocity of 3.76/min). Off-gas from the oil shale runs required significant treatment. The flow diagram in Fig. 4 shows the sequence of cooling, condensing, filtering and precipitation on NaOH pellets (to collect gas contaminants, principally H_2S and CO_2 gases). Thereafter the gas was evacuated by vacuum pump and discarded.

Mensuration: Weight measurements were taken on one of two balances: a 200 gram capacity, 0.1 milligram sensitivity; and a 1 kilogram capacity, 0.01 gram sensitivity units. In one run (Indiana #2) the center auger blade was inadvertently omitted from the run. This slowed the heating rate and heat conductance, however, the product yield was fairly good for the run. Oil density was determined with a 10 cc pycnometer. Oil pour point was determined to the nearest $5^{\circ}F$. Alkalinity or pH was measured with Micro Essential Labs pHydriion paper measuring in the pH range of 1 to 11. Sieving measurements were obtained in an 8" sieving set and 30 minute shake period. Sieve sizes are shown in Appendix D.

Sample Analysis

Analysts: Chemical analyses and Fischer Assay were performed by Western Research Institute (WRI). All samples were submitted to WRI together, to optimize the sample analysis uniformity. Rock density and Thermogravimetric analyses (TGA) were performed at the University of Utah Experimental Survey. Weight, volume, density, pour point, pH and sieving measurements on the feed for the runs and the products from the runs were made with Energy Recovery Tech. equipment and personnel. All the analytical and weight data on samples and runs are summarized in Appendices A, B and C. TGA data were used as a guide, primarily in the oxidation runs and are included as Appendix G.

Raw Oil Shale: One secondary (1 Kg) sample from each primary (20 kg) sample of raw oil shale was riffle-divided into 500 gram samples, one to be analyzed for Fisher Assay. Approximately 100 grams were riffle-divided from the rest of each secondary sample. The 100 gram sample was ground to -20 mesh and a 10 gram sample divided out. The 10 gram sample was further ground to -100 mesh.⁵ Finally, samples (2 grams each) of the -100 mesh ore were submitted for Total Carbon, Hydrogen and Nitrogen (CHN) and Mineral Carbon analyses. Our main interest was in the Organic Carbon, (i.e. the difference between the Total Carbon and Mineral Carbon) and the Fisher Assay. The sum of Organic Carbon plus Hydrogen plus Nitrogen can provide a low estimate of the organic matter in a sample. The estimate would be low because it would not include organic sulfur and oxygen.⁶

Retorted Oil Shale and Ash: Samples were prepared by grinding and subdividing as was described above. Samples of 2 grams from one or more oil shale runs and one ash sample from each of the five oil shale samples were submitted to WRI for analysis.

RESULTS AND DISCUSSION

Heat Transfer--Sand Runs: In the batch rotary kiln, heat is transferred from the furnace to the kiln wall and from the wall to the inner contents of the kiln. The temperatures for a typical run wherein the furnace was programmed to heat immediately to the maximum temperature is plotted in Fig. 5. It can be observed from this figure how the heating rate (slope) of kiln wall temperature vs time, is proportional to the temperature difference between the wall and the furnace. Note that at about 6 minutes, where the furnace temperature levels off, the point of maximum temperature difference between the wall and the furnace is also the point of steepest slope for the kiln heating rate. Similarly, the heating rate of the inner kiln contents is proportional to the temperature difference between the kiln wall and the inner kiln contents.

Mathematical Model: An Unsteady State Heat Analysis of the rotary kiln allows us to obtain the Coefficient of Heat Transfer for the system: During the time moment, dt , the sand heats dT_s . Some of the heat transfers from the sand to the inner kiln (auger blade assembly) and the inner assembly heats dT_A . Assuming that the internal kiln temperature increment, dT_A , will be proportional to dT_s , then $dT_A = k dT_s$. The increase in sand energy in time moment, dt , is given by:

Change in Sand Energy = Heat Flow to Sand - Heat Flow to Inner auger

Thus: $m_s c_s dT_s = U A F_C \Delta T dt - m_A c_A k dT_s$ (1)

Where T = Temp. ($^{\circ}\text{F}$)

ΔT = Delta T = Wall Temp. - Sand Temp.

U = Thermal Conductance from the kiln wall to the sand ($\text{Btu/hr/ft}^2/^{\circ}\text{F}$)

t = Time (hr or min)

A = Total area of kiln wall = 1.479 ft^2

F_C = Effective Covering Fraction of the kiln wall by the sand (see Appendix A)

m_s = Mass (lb) of sand (see run summary in Appendix A)

m_A = Mass (lb) of auger blade assembly = 1.3 lb

c = Specific Heat. For quartz and steel, averages are 0.25 and $0.12 \text{ Btu/lb/}^{\circ}\text{F}$, respectively. Equivalent Specific Heat oil shale pyrolysis calculated from data in RI-7482: $c_{\text{oil shale}} = .33$ to $.36$. k relates the heating rate of the interior metal to the heating rate of the sand ($k \approx 1$).

Differential values, dT & dt , are defined above.

Equation (1) can be rearranged, to illustrate the slope, as follows:

$$\text{slope} = (dT/dt)/\Delta T = UAF_C/(m_s c_s + m_A c_A k) \quad (2)$$

The slope of the sand temperature vs time, in the previous Fig. 5, corresponds to the heating rate, dT/dt . If that heating rate is plotted vs Delta T (the Wall minus Sand Temperature), the result is the Fig. 6 curve with the same slope as on the left side of equation (2). On the right side of the equation, values for A , F_c , m , c and k are known. Thus U can be calculated.

Radiation Effect: The graph of sand Heating Rate vs ΔT (Fig. 6) exhibits a curious loop reminiscent of a hysteresis loop. Heating Rate and ΔT both begin near 0 as the run starts at room temperature (Low Range).

The curve increases to a maximum

corresponding to the maximum heating rate (6 minutes, as noted in Fig. 5), during which the curve is undergoing a transition to a higher slope. As the furnace continues to heat past the maximum heating rate, the curve of Heating Rate vs ΔT decreases and approaches 0 again as the kiln temperature equilibrates at the control temperature (1000°F). The reason for the higher slope of the high temperature range (vs the low range) of Fig. 6 appears to be due primarily to the contribution from radiation at the higher temperatures.

To illustrate radiant heat transfer, we can add a radiation term, as a part of U , in equation (2). This term will then allow for the separation of effects of conduction and radiation. The term, $A\epsilon\sigma[T_{\text{Wall}}^4 - T_{\text{Sand}}^4]$, can be included, where T is the wall and sand temperatures, A is the area exposed to radiation, ϵ is the net emissivity of internal surfaces and ranges from 0 to 1, σ is the Stefan-Boltzmann constant, 0.172×10^{-8} . It is convenient to divide the fourth power of absolute temperature by 10^8 , or 100^4 , and we have:

$$\text{Radiation} = e[(T_{\text{Wall}}/100)^4 - (T_{\text{Sand}}/100)^4]$$

$A\epsilon$ and the antecedent of the σ exponent, 0.172, are combined into a single constant, e , which must be determined by experimentation, as the value providing the straightest conductivity curve. The conductivity curve is then expressed as:

$$\text{SLOPE}_{\text{COND}} = \{dT/dt - e[(T_{\text{Wall}}/100)^4 - (T_{\text{Sand}}/100)^4]/(m_s c_s + m_a c_a k)\}/\Delta T$$

The resulting slope (Fig. 7) due to simple conductance is a straight line for all but an initial period of the low temperature leg, during which the system dynamics may not have been established.

Heat Transfer Coefficient: To calculate the heat transfer coefficient, U , it is helpful to rearrange equation (2):

$$U = \text{Slope } (m_s c_s + m_a c_a k) / (A F_c) \quad (3)$$

Coefficient, U , was determined from the total average slope, as in Fig. 6, for over 50 sand runs made during this project. Values of U vs Kiln Surface Velocity are plotted in Fig. 8. For comparison, the empirical data of Sullivan and Sabersky (discussed below) have been included. These runs were primarily 2 pound loads to establish the curve for the total velocity range. Runs with 1 and 4 lb loads were also made to observe the effect of run size. (Appendix A summarizes all the run conditions and data used to calculate U .) Figure 8 is helpful to observe the effects of kiln velocity on heat transfer. Heat Transfer Coefficient increases rapidly with increase in Kiln Velocity

up to about 140 ft/min where the curve peaks at about 107 Btu/hr/ft²/°F (4 lb load). At higher velocity the curve turns downward rapidly.

The reason for the decrease in heat transfer at high kiln velocity is due to two effects: (1) centrifugation which causes reduced sand mixing (the largest effect), and (2) shallow bed effects which cause reduced wall-particle contact.

Centrifugation: The critical surface velocity, V_c , is the velocity where flow of particles (sliding down the upwardly moving kiln surface) is disrupted by centrifugation whereupon the kiln contents are taken along with the moving wall. Centrifugation occurs above a V_c that is a function of the kiln diameter or position that a particle is held from the kiln center. Fig. 9 is a graph of

equivalent critical velocity functions: $V_{\text{CRITICAL}} = 241(\text{Diam})^{1/2}$ ft/min, and

$RPM_{CRITICAL} = [5873(ft/min^2)/Diam(ft)]^{1/2}$. The RPM_C curve shows that although centrifugation may begin at the kiln surface, e.g. at 115 RPM near the maximum kiln diameter of 5.4", particles may still flow and mix at positions closer to the kiln center not yet at critical RPM. For example at a position 1/2" from the wall, diameter = 4.4" and RPM_C is 127. So although particles begin centrifuging at the surface (5.4"), flow may still continue at higher RPM nearer the center. Thus heat transfer in Fig. 9 is reducing rapidly at V_C of 160 but the slope continues beyond 160 ft/min. Surface irregularities in the kiln (e.g. leading edges of auger blades and thermocouples) may tend to cause centrifugation at lower RPM than would occur without the irregularities. This point is significant to this project because the auger blades are a smoother design than was used in 1987, consequently the heat transfer peak is shifted to a higher RPM.

Rutgers has described mechanisms of bed motion in a horizontal cylindrical kiln in terms of the ratio of kiln RPM to the critical RPM_C . He showed that effects and flow regimes can be predicted on the basis of this ratio. The peak at 140 ft/min is 87% of the critical velocity of 160 ft/min and it is likely that this fraction is significant for the auger assembly, or similar one, used in this or similar kilns.⁷

Shallow Bed Phenomena: Data for Heat Conductance of particles flowing on a flat plate, Fig. 10, is reconstructed from data of Sullivan and Sabersky, and Spelt et al.^{8,9} They refer to the work of Botterill and Desai¹⁰ who previously noted that the particle packing density near the wall is a governing factor

for heat transfer to fluidized or flowing beds. Spelt et al. note that as velocity increases, at some point the increasing particle mobility is accompanied by a decrease in packing density and heat transfer. Thus as velocity increases, in Fig. 10, the heat transfer reaches a maximum and then curves downward. The greater pressure from larger bed depths tends to maintain the packing density and so accounts for the higher peaks for deeper beds.

Although centrifugation counteracts the reduced packing density to a degree, it appears that the latter effect may account for the low heat transfer values for small loads (1 & 2 lb loads), as observed in Fig. 8. A normalizing feature can be included in equation (2) so 1 and 2 pound load curves can be normalized to the 4 pound curves by raising F_C to a power, F_C^P . We normalize to the larger load data since our interest is in larger kilns (and deeper beds). A statistical procedure helped to

accurately establish the value (of $P = 1.25$) to minimize the data spread. A constant, $C = 0.8$, counter-adjusts the magnitude of U which would otherwise increase with increasing P . Thus we have equation (3) which was used to calculate the results in Fig. 11 wherein the three different load sizes fall in the same range.

$$U = C \text{ Slope } (m_s c_s + m_A c_A k) / (A F_C^P) \quad (3)$$

Heat Transfer--Oil Shale Runs: Twelve retorting runs were made on the five different oil shales in the kiln. The average heat transfer in the rotary kiln was 78 Btu/hr/ft²/°F for 8 Green River runs. It was 74 for 3 Eastern oil shales. Heat transfer for the retorted oil shale combustion is included in Fig. 11 and is very close to the same value for Green River oil shale retorting. The average net heat transfer in the continuous process kiln (with oil shale on the inside of the Heat Conducting Wall and burning spent oil shale outside a 1/16" stainless steel wall) net heat transfer would be 38 Btu/hr/ft²/°F. This is about 5% lower than previous estimates.¹¹

In this context, Fig. 9 also illustrates that the critical velocity increases with increasing kiln diameter. Note that a 12" diameter kiln has a V_C of 241 ft/min. Deep particle beds in larger kilns and intense mixing that occurs in rotating kilns will add to the effects promoting heat transfer. On the basis of the empirical relation of Sullivan and Sabersky (Fig. 11) ultimate CHESS process heat transfer may possibly increase by 20% or more above the values observed for this small kiln. If so it would increase net heat transfer from 38 to the range of 40 to 50 Btu/hr/ft²/°F.

	Oil Yield	Oil Density	Gas
Occidental 2	111	103	59
Occidental 3	108	103	75
Occidental 4	109	103	52
Parachute 1	110	104	85
Parachute 2	112	104	90
Tipton 1	103	106	82
Tipton 2	106	105	65
Tipton 3	105	105	86
Kentucky 1	114	106	46
Kentucky 2	117	105	59
Indiana 1	106	106	79
Indiana 2	102	106	76
AVG. % of F.A.	108.6	105	71

Oil Shale Retorting

High Oil Yield: One of the very positive results of this project is the demonstration of high oil yield. Average oil yield was 108.6% of Fischer Assay. All 12 oil shale runs were significantly higher yield than Fisher Assay. The lowest yield was the Indiana #2 run, at 102% of Fischer Assay, possibly because it

was an irregular run, as was noted previously. However, for oil yield, Indiana #2 was averaged together with the other runs.

High oil yield is also indicated, in the Table I summary results (of Appendices B and C), by two additional sets of data which are consistent with high oil yield. These are high Oil Density and low Gas production. These three effects are all indications of a low degree of oil reforming and cracking. These are the natural result of the rotary kiln system with ample mixing, good gas-solid contacting and an effective sweepgas - features absent from the Fischer Assay system. Additional CHESSE kiln effects common to the Fischer Assay but not common to recycled ash systems are: the momentous absence of the high surface area of the coke-promoting hot recycle ash; and the immediate evacuation and cooling of the oil vapor at

relatively low temperatures (the formation temperature from 700° to 900°F vs about 1300°F for hot recycled ash). All the analytical data for the oil shale samples before and after retorting and after oxidation runs are included in Appendix C.

Kiln Plugging Tendency was defined in the 1987 Tar Sand project as the percent of residual solids that adheres firmly to the kiln at the end of the run. In the Tar sand runs, plugging percentages ranged from 3 to 25%. The most important finding of this work is that all of the 12 oil shale runs exhibited zero plugging tendency or a complete absence of any kiln surface-adhering solids. This is positive

information for the success of the Adams CHESSE kiln and it confirms and extends the limited oil shale data (one oil shale run) of the 1987 tar sands project.

Particle agglomeration and growth, if it should occur to a great extent, is a second kind of plugging, that could occur in the CHESSE kiln. To show that agglomeration would not occur when processing various ores, size distribution of the samples was determined for each ore before and after retorting and after burning. All retorted samples exhibited the tendency illustrated in Fig. 12 for Occidental oil shale (see Appendix D), wherein the particle distribution shifted slightly toward smaller particles during retorting. Although particles are known to agglomerate in packed bed retorts, we should anticipate no plugging due to particle agglomeration in the rotary kiln.

Spent Oil Shale Coke Combustion¹²: Five spent oil shale runs, one run with each of the five oil shales, were burned in a variable mixture of nitrogen and air. The runs were first taken to 1000°F in 100% nitrogen. Then gradually increasing amounts of air were mixed with the nitrogen sweep gas in a program to simulate the continuous process kiln, as shown in Fig. 12 for oxidation of Kentucky spent shale. In the CHES process kiln, the newly retorted oil shale contacts a lean air mixture in combustion gas. The mixture gradually becomes richer in air as the burning shale flows counter-current to the feed air.

Carbon Conversion-Pyrolysis: Table II provides a summary of (Appendices C and G), carbon conversion data for retorting and combustion runs in the kiln. Retorting normally converts 73 to 81% of Green River oil shale carbon to liquid and gas, the rest remaining in the spent shale as coke. Singleton et al. have shown that Green River oil shale conversion is moderately dependant on the ore grade, lean grades converting a lower percentage of the kerogen.¹³ That effect is borne out in this study. Column B shows the carbon converted by retorting. The low grade ores converted the lowest percentage of organic carbon (in the order: Occidental < Tipton < Parachute).

Coke oxidation: The percent of the spent shale carbon that was converted by combustion

	A	B	C	D	E	F
Sample	Grade (gpt)	% RSOC Retorted	% SSOC Burned	Tot. RSOC Reacted	Min. Grade	% C XCES
Occidental	18.2	76	69	92	14.1	30
Parachute	28.2	81	69	94	14.1	100
Tipton	20.3	79	60	91	19.3	5
Kentucky	13.4	48	55	77	2.1	540
Indiana	13.9	48	21	59	7.8	80

Column A: Fisher Assay sample grade. Column B: Pyrolysis removed Raw Shale Org. C. Column C: % of Spent Shale Org. Carbon that was burned (spent shale basis). Column D: % of Total Carbon pyrolyzed + burned (raw shale basis). Column E: minimum oil shale grade that will provide adequate process heat based on conversion in Col. C. Column F: % Excess Carbon = $100(\text{Col. A}/\text{Col. E})$

is given in Column C and indicates the efficiency of the combustion. Two limitations of the combustion were the size of the particles during combustion and inactivity of the Eastern oil shale residue. The larger particles (3 mm) were dark in the center and light near the surface indicating complete burning occurred at the particle periphery but not in the center. The particles smaller than 1 mm appeared to have burned more completely. This observation

may indicate that for applications where complete carbon combustion is desired, the particle size should be approximately 1 mm and smaller.

A smaller maximum size will not markedly detract from the claim of relatively large effluent particle size for the CHES process. For although the maximum size may be smaller than previously anticipated, the process fines will still be relatively fewer as compared to recycled ash conditions that generate fines. These conditions are: (1) rapid particle heatup which causes particle-bursting decrepitation, and (2) high temperature, above 1000°F, where the mineral carbonates decompose to ultra-fine particles. It has been noted by Barney and Carlson "Upon decomposition of the carbonates, the residue or shale ash is converted to an extremely fine (50-90 wt. % -44 micron), porous and oleophilic material.¹⁴ And of course, it is the very fine particles that are difficult to manage.

It is anticipated that by adjusting the maximum particle size and using the appropriately higher temperature, in the case of Eastern shales, the burning efficiency will be much higher, possibly 90% or above.

Excess Process Heat: All the ashing runs exhibited excess heat for the CHES process. Although the Eastern oil shales are very low oil grade, the spent shales are carbon rich.

Even with very low carbon oxidation of 21%, the Indiana sample still had 80 % excess heat. (Note the explanations at the table bottom. The calculations for Column E are provided in Appendix G.)

The degree of oxidation of the carbon on the spent shale, though less than 100%, is still a momentous success, showing that the carbon on lean grade ores can drive the CHESS process and provide excess heat. The degree to which the coke in the runs was oxidized was also a function of the oil shale type and oxidizing temperatures. While 1000°F will be adequately hot to process Green River oil shale, some Eastern oil shales will probably need to be oxidized at temperatures 100-300 degrees hotter for complete oxidation of the coke.

Ash Alkalinity: Before processing, the alkalinity for all five oil shale samples was neutral (pH = 7). Upon processing, the ash pH increased to 9 and 11 for the Parachute and Tipton samples respectively. All the other samples, Occidental, Kentucky and Indiana, had not changed pH. While all the Green River oil shales have a large fraction of mineral carbonates, they would be only slightly affected below 1000°F, as was the Occidental sample. The Parachute sample maximum temperature was 1037°F during pyrolysis (Appendix B) which may have caused some carbonate calcination to account for the raised pH of 9. The Tipton sample maximum was only 1000°F. The thermogravimetric analysis of the Tipton sample had a weight loss peak at about 600°F, before the hydrocarbon peak began to evolve and this seems to indicate the presence of a mineral such as dawsonite. Dawsonite would decompose at around 600°F to form sodium carbonate and could possibly account for the high pH of 11. Dawsonite is a desirable aluminum ore and would likely be removed prior to retorting if it is found in significantly large amounts. Careful control of the process below 1000°F should produce product ash of desirably low alkalinity.

Environmental Impact

CHESS process heat recovery will reduce the combustion product by the same amount as the heat recovered, 80 to 90% of process heat (see Appendix G). Scrubbers and gas cleanup requirements will thus be greatly reduced for the CHESS process. Low temperature pyrolysis and combustion will minimize the alkaline calcination of mineral carbonates in Western oil shales. Combustion of the coke on the spent shale will help strip the polyaromatic hydrocarbons from the ash and reduce the amount of this known contaminant.¹⁵ Where other processes would depend on water cooling, Counter-current heat exchange in solid streams will markedly conserve water. Thus, lower heat requirements and the low temperature of the CHESS process equate to the mitigation of the environmental impact of oil shale processing.

Needed Development: The U.S. imports nearly 3 billion barrels of oil, at a cost of over \$50 billion per year, causing a strain on the U.S. balance of payments and jeopardizing our national security. The demand for oil is increasing as world oil supplies, especially the domestic share, are decreasing. It is estimated that U.S. production will decrease 80% by the year 2010.¹⁶ Increasing oil prices, gradual or sudden, are inevitable, probably within the next ten to fifteen years. Ample resources are available in the Green River oil shale reserves to supply the U.S. needs for over a hundred years.

The CHESS process has the potential to develop shale oil more economically and with less environmental impact than other current methods. The demonstration of this new shale oil technology, from the Process Development Unit (PDU) to Demonstration Plant stage

would require approximately ten years. With the success of the current project research, construction of a small PDU is necessary to demonstrate the CHES process features in a continuously operating unit.

CONCLUSIONS

The following observations, in order of importance to the success of the CHES process, can be made at the conclusion of this phase of the project:

(1) All of the oil shale runs, 12 operational, as well as all preliminary debugging oil shale runs, were attended by a complete absence of kiln surface-adhering solids. There was no particle agglomeration in any of the runs.

(2) Process simulation runs burned 60 to 70% of the coke from the Green River spent oil shales and 20 to 55% of the Eastern spent oil shales. This level would provide ample heat for processing oil shales of 20 gal/ton and much leaner after process optimization.

(3) The overall Heat Transfer Coefficient for the Process Development kiln (1/16" wall) will be in the range of 40 to 45 Btu/hr/ft²/°F.

(4) Average oil yield was (a desirably high) 108.6% of Fisher Assay.

(5) Calculations indicate that this level of heat transfer will provide for 80% of the heat requirements and spent shale coke combustion can provide for the other 20%, with much heat to spare, even with very lean oil shale grades.

(6) The success of the above features predicts an environment-friendly shale oil recovery process.

With the demonstration of these positive features, the immediate imperative is to go forward with the development of a continuous process development.

NOTES AND REFERENCES

1. The CHESS process was formerly referred to as Counter Current Solid Streams Heat Transfer (CCSSHT). The name was changed in response to the suggestion of one of the principals at the 1991 DOE sponsored Commercialization Workshop (Austin, Texas), that the process needed a better name. More than an easier to pronounce acronym, the name "CHESS" brings to mind an intellectual, strategically designed approach. So the name is appropriate to this process, the only oil shale process designed at the outset for efficiency. It is an obvious fact that heat recovery must be a big part of any successful oil shale process. Nevertheless, most shale oil process designs relegate heat recovery to an afterthought position, a unit operations add-on, after everything else is considered. Except for the CHESS process, only the Taciuk retort uses heat recovery as an integral part of the retort. But the Taciuk retort recycles the hot ash (a co-current operation) and recovers heat only in a minor and inefficient way.
2. Abstracts of the 1987 and 1990 projects were published in *Small Business Innovation Research, Abstracts of Phase I Awards*, SBIR Program Mgr., Office of Energy Research, U.S. DOE, Wash., D.C. 20545. 1987, page 45, and 1990, page 16. The project reports are available through NTIS (3 yrs. after submission, i.e. 1991 and 1994), or by contacting Energy Recov. Tech., 886 Monument Park Circle, SLC, UT 84108.
3. For details of the CHESS Retort design, see D. C. Adams, *A High Efficiency Retort to Recover Shale Oil, A Proposal for an R & D Project to Demonstrate the Feasibility of a High Efficiency Oil Shale Kiln*; Submitted to the NIST, December 1989, Recommendation # 533, DOE OERI # 013721.
4. M. Desai, Ph.D. Dissertation, Univ. of Birmingham, England (1970).
5. This elaborate chain of grinding and subdividing in multiple stages is to provide ample fine particles after subsequently subdividing the heterogeneous material. This care was used to ensure that a subdivided sample be fine enough so that even if all the particles were maximum size from the sieve, at least 10,000 particles would be in the subdivision to promote high probability of uniformity between samples, or that the subdivided sample would be representative of the larger sample. The fine size of -100 mesh was requested by WRI for their analyses of CHN & Mineral Carbon. This fine size is consistent with a 10,000 particle sample if the CHN samples are no smaller than 33 milligrams.
6. Measurement of organic sulfur and oxygen presents a significant problem beyond the scope and need of this project. Organic sulfur is usually obtained by first determining the total sulfur then subtracting determinations of the different forms of mineral sulfur, primarily pyrite (FeS_2) and sulfates (e.g. CaSO_4), sometimes including traces of marcasite (FeS_2) and pyrrhotite or toilitite (FeS). Organic sulfur is normally a small fraction, less than 1% of oil shale and in one sample it was just 1% of the kerogen content. But it varies greatly perhaps as a result of the proximity to mineral sulfur. Organic oxygen presents an even greater problem. It is usually determined by subtracting the non-oxygen components from the total

weight. Thus the error of the oxygen analysis would contain the sum of all the error including any mineral nitrogen, which is sometimes present.

7. R. Rutgers, Chem. Eng. Sci. **20**, 1089, (1965). It should be noted that the 1987 project used a very different auger assembly. It used multiple short auger blade sections, no center auger blade and the kiln was set at a 7° angle to promote flow through the center. Not surprisingly, the peak heat transfer occurred at a low 40% of the critical velocity.

8. W. N. Sullivan and R. H. Sabersky, *Int. J. Heat Mass transfer* Vol. **18**. pp. 97-107, (1973).

9. J. K. Spelt, et al. "Heat Transfer to Flowing Granular Material," *Int. J. Heat Mass Transfer*. Vol. **25**, No. 6. 791-796 (1982). This study was for glass beads on a flat plate but it extended the data of Sullivan and Sabersky to higher surface velocities.

10. J. S. M. Botterill, and M. Desai, "Limiting factors in gas-fluidized bed heat transfer," *Powder Technology*, **6**, 231 (1972).

11. A value of 40 Btu/hr/ft²/°F was previously estimated in Appendix B of the project proposal, Ref. 3.

12. As used in this report the words "combustion" and "burn" should be understood in the alternate dictionary sense of "slow oxidation and little light."

13. M.F. Singleton, et al. *Assay Products from Green River Oil Shale*, UCRL-53273, Rev. 1 (1986).

14. J. H. Barney and F. B. Carlson, Quoted in *Oil from Shale and Tar Sands*, E. M. Perrini, Noyes Data Corp. 1975, p. 93.

15. For example, see discussion by J. J. Schmidt-Collerus, *The Disposal and Environmental Effects of Carbonaceous Solid Wastes from Commercial Oil Shale Operations*, Denver Res. Inst., Jan. 1974. NTIS Doc. # PB-231 796.

16. H. Robb, *Final Technical Review; A High Efficiency Retort To Recovery Shale Oil*, OERI # 13721, page 2. See Proposal, Ref. 3.

APPENDIX A: SUMMARY OF KILN RUN HEAT TRANSFER CALCULATION DATA

Material	Run & File #	Solids Load (lb)	Solids Bulk Dens (lb/in ³)	Solids Volume (Culn)	Filled Fraction Ff	Covered Fraction Fc	Slope (Ht. Rate vs Delta T)	RPM	Surface Velocity (Ft/min)	Ht. Trans. Coef. (U)
SAND RUNS										
Quartz Sand	921007S1	2.203	0.048	46.0	0.202	0.309	0.523	5	7	52
Quartz Sand	921204S1	2.203	0.048	46.0	0.202	0.309	0.533	7	10	53
Quartz Sand	921008S5	2.203	0.048	46.0	0.202	0.309	0.609	15	21	61
Quartz Sand	921202S2	2.203	0.048	46.0	0.202	0.309	0.660	20	28	66
Quartz Sand	921028S2	2.203	0.048	46.0	0.202	0.309	0.702	24	33	70
Quartz Sand	921009S1	2.203	0.048	46.0	0.202	0.309	0.673	25	35	67
Quartz Sand	920922S1	2.203	0.048	46.0	0.202	0.309	0.726	28	39	73
Quartz Sand	921031S1	2.203	0.048	46.0	0.202	0.309	0.895	42	63	90
Quartz Sand	921009S2	2.203	0.048	46.0	0.202	0.309	0.800	36	51	80
Quartz Sand	921027S1	2.203	0.048	46.0	0.202	0.309	0.864	45	63	86
Quartz Sand	921012S2	2.203	0.048	46.0	0.202	0.309	0.937	46	65	94
Quartz Sand	921119S2	2.203	0.048	46.0	0.202	0.309	0.965	56	79	97
Quartz Sand	921010S1	2.203	0.048	46.0	0.202	0.309	0.966	60	85	97
Quartz Sand	921030S4	2.203	0.048	46.0	0.202	0.309	0.934	62	85	93
Quartz Sand	921030S3	2.203	0.048	46.0	0.202	0.309	0.987	64	90	99
Quartz Sand	921102S2	2.203	0.048	46.0	0.202	0.309	0.978	68	96	98
Quartz Sand	921118S1	2.203	0.048	46.0	0.202	0.309	1.041	78	110	104
Quartz Sand	921106S1	2.203	0.048	46.0	0.202	0.309	1.011	80	112	101
Quartz Sand	921130S1	2.203	0.048	46.0	0.202	0.309	1.010	81	114	101
Quartz Sand	921029S1	2.203	0.048	46.0	0.202	0.309	1.020	82	116	102
Quartz Sand	921008S1	2.203	0.048	46.0	0.202	0.309	1.010	85	120	101
Quartz Sand	921130S2	2.203	0.048	46.0	0.202	0.309	1.072	91	128	107
Quartz Sand	921102S1	2.203	0.048	46.0	0.202	0.309	1.030	93	131	103
Quartz Sand	921103S2	2.203	0.048	46.0	0.202	0.309	1.090	96	135	109
Quartz Sand	921118S3	2.203	0.048	46.0	0.202	0.309	1.054	99	140	105
Quartz Sand	921201S1	2.203	0.048	46.0	0.202	0.309	1.062	99	140	106
Quartz Sand	921120S1	2.203	0.048	46.0	0.202	0.309	1.047	105	148	105
Quartz Sand	921107S1	2.203	0.048	46.0	0.202	0.309	1.070	106	149	107
Quartz Sand	921118S4	2.203	0.048	46.0	0.202	0.309	1.028	106	149	103
Quartz Sand	921103S1	2.203	0.048	46.0	0.202	0.309	1.068	107	151	107
Quartz Sand	921202S1	2.203	0.048	46.0	0.202	0.309	0.993	110	155	99
Quartz Sand	921103S3	2.203	0.048	46.0	0.202	0.309	1.064	115	162	106
Quartz Sand	921119S1	2.203	0.048	46.0	0.202	0.309	0.937	120	169	94
Quartz Sand	921104S1	2.203	0.048	46.0	0.202	0.309	0.920	122	172	92
Quartz Sand	921105S1	2.203	0.048	46.0	0.202	0.309	0.785	127	179	79
Quartz Sand	921203S1	2.203	0.048	46.0	0.202	0.309	0.636	139	196	64
Quartz Sand	921030S1	2.203	0.048	46.0	0.202	0.309	0.446	150	212	45
Quartz Sand	921228S1	3.982	0.048	83.1	0.365	0.418	0.898	77	109	101
Quartz Sand	921228S2	3.982	0.048	83.1	0.365	0.418	0.972	99	140	111
Quartz Sand	921227S1	3.982	0.048	83.1	0.365	0.418	0.829	60	85	93
Quartz Sand	921227S2	3.982	0.048	83.1	0.365	0.418	0.730	38	54	82
Quartz Sand	921227S3	3.982	0.048	83.1	0.365	0.418	0.765	122	172	86
Quartz Sand	921229S1	3.982	0.048	83.1	0.365	0.418	0.952	100	141	107
Quartz Sand	921229S2	3.982	0.048	83.1	0.365	0.418	0.960	111	157	107
Quartz Sand	921229S3	3.982	0.048	83.1	0.365	0.418	0.944	80	113	106
Quartz Sand	921230S1	3.982	0.048	83.1	0.365	0.418	0.873	57	80	98
Quartz Sand	921230S2	3.982	0.048	83.1	0.365	0.418	0.860	58	82	96
Quartz Sand	930213S1	1.322	0.048	27.6	0.121	0.244	1.020	63	89	94
Quartz Sand	930213S2	1.322	0.048	27.6	0.121	0.244	1.110	77	109	102
Quartz Sand	930213S3	1.322	0.048	27.6	0.121	0.244	1.110	83	117	102
Quartz Sand	930213S4	1.322	0.048	27.6	0.121	0.244	1.140	103	145	109
OIL SHALE AND O.S. RESIDUE (ASH) RUNS										
Occidental 2	930105X2	2.226	0.038	58.7	0.258	0.348	0.672	88	124	74
Occidental 3	930210X3	2.282	0.038	60.2	0.265	0.353	0.697	87	123	77
Occidental 4	930219X4	2.146	0.038	56.6	0.249	0.342	0.707	89	125	77
Parachute 1	930306P1	2.127	0.037	57.6	0.253	0.345	0.730	95	134	83
Parachute 2	930310P2	2.227	0.037	60.3	0.265	0.353	0.696	90	127	80
Tipton 1	930312T1	2.143	0.037	58.2	0.256	0.347	0.743	97	137	81
Tipton 2	930316T2	2.114	0.037	57.4	0.252	0.344	0.700	95	134	76
Tipton 3	930317T3	2.019	0.037	54.8	0.241	0.337	0.730	90	127	78
Kentucky 1	930226E1	2.405	0.039	61.8	0.272	0.357	0.660	90	127	74
Kentucky 2	930303E2	2.235	0.039	57.5	0.253	0.345	0.666	91	128	74
Indiana 1	930320I1	2.167	0.038	57.7	0.254	0.345	0.666	96	135	73
Indiana 2	930323I2	2.183	0.038	58.1	0.256	0.346	0.530	95	134	57
Occidental Ash	930327XA	1.636	0.042	38.7	0.170	0.285	0.812	93	131	82
Parachute Ash	930615PA	1.323	0.038	35.2	0.155	0.273	0.805	93	131	74
Tipton Ash	930616TA	1.773	0.039	45.4	0.200	0.307	0.790	95	132	77
Kentucky Ash	930622KA	1.960	0.040	48.9	0.215	0.318	0.820	97	137	83
Indiana Ash	930628IA	1.704	0.036	46.7	0.205	0.311	0.800	93	131	75

Average U = 78, 74 & 78 Btu/hr/ft²/°F for 8 Green River & 3 Eastern oil shales & 5 spent oil shale runs, respectively. Run 930323I2 (Indiana 2) excluded.

APPENDIX B

SUMMARY OF PYROLYSIS RUN FEED AND PRODUCT DATA

1993 OIL SHALE RUNS IN ROTARY KILN

Run	Shale	Residue	Weight	Condensate		NaOH	Line	Tot. Liq.	Gas	Gas as % of Gas + Liquid
				Bottle	Mist					
	(< ----- Grams ----- >)									
Occidental 2	1000.35	887.71	112.64	55.47	17.21	20.61	4.28	97.57	15.07	13.4
Occidental 3	1034.78	920.20	114.58	45.64	20.22	21.24	7.72	94.82	19.76	17.2
Occidental 4	973.17	863.16	110.01	50.53	13.81	22.78	9.86	96.98	13.03	11.8
Parachute 1	965.16	780.20	184.96	101.74	8.22	23.16	2.70	135.82	49.14	26.6
Parachute 2	1009.88	822.20	187.68	109.03	7.38	23*	4.95	144	43*	23*
Tipton 1	972.17	815.63	156.54	99.96	9.30	17.45	6.42	133.13	23.41	15.0
Tipton 2	959.04	805.97	153.07	98*	11.86	18.70	6.20	135*	18*	12*
Tipton 3	916.24	764.47	151.77	97.51	9.84	14.13	6.10	127.58	24.19	15.9
Kentucky 1	1090.91	966.08	124.83	62.98	14.00	20.60	10.20	107.78	17.05	13.7
Kentucky 2	1013.66	888.11	125.55	67.85	12.30	18.58	4.80	103.53	22.02	17.5
Indiana 1	982.53	854.61	127.92	72.31	11.40	17.96	4.62	106.29	21.63	16.9
Indiana 2	990.04	867.30	122.74	75.59	12.37	10.04	4.86	102.86	19.88	16.2
Run Sample	Ore Fischer Assay	Oil Density	Oil Yield	Oil Yield	Relative Oil Yield†	Oil Pour Point	Percent Reacted	Minutes Above 900F	Maximum Temper- ature	Plugging Tendenc
	(gpt)	(g/ml)	(ml)	(gpt)	(% of FA)	(deg. F)	(%)	(min)	(deg. F)	(%)
Occidental	17.81	0.948	82	19.8	111	70	11.3	16	997	0
Occidental	17.36	0.948	81	18.8	108	70	11.1	11	1009	0
Occidental	18.64	0.946	82	20.2	109	70	11.3	16	959	0
Parachute 1	28.14	0.924	125	31.1	110	95	19.2	16	1037	0
Parachute 2	28.25	0.923	133	31.6	112	95	18.6	9	1013	0
Tipton 1	20.27	0.964	84	20.8	103	40	16.1	10	956	0
Tipton 2	20.27	0.962	86	21.4	106	40	16.0	8	999	0
Tipton 3	20.30	0.960	81	21.2	105	40	16.6	14	959	0
Kentucky 1	13.36	0.998	69	15.2	114	0F	11.4	15	938	0
Kentucky 2	13.43	0.998	66	15.7	117	0F	12.4	20	999	0
Indiana 1	13.89	0.993	60	14.8	106	5F	13.0	16	982	0
Indiana 2	13.89	0.993	59	14.2	102	5F	12.4	9	975	0

*Data were affected by inexact measurements in two runs. Decimals indicate accuracy level.
†Average Relative Oil Yield is 108.0 and 109.5 % of Fisher Assay for 8 Green River and 4 Eastern oil shales, respectively.

APPENDIX C

SUMMARY OF ANALYTICAL DATA: RAW SHALE, SPENT SHALE & ASH 1993 OIL SHALE RUNS IN ROTARY KILN

Oil Shale Sample			Occidental		Parachute		Tipton		Kentucky		Indian
			#2	#3	#1	#2	#1	#3	#1	#2	#1
FISCHER ASSAY OF RAW SHALE											
1	Spent Shale	(%)	88.99	89.02	83.18	82.52	84.46	84.40	88.18	88.10	87.77
2	Oil Weight	(%)	6.82	6.92	10.46	10.45	7.71	7.73	5.29	5.29	5.44
3	Gas + Loss	(%)	2.50	2.52	4.56	5.14	2.86	2.88	3.53	3.61	2.61
4	Water Weight	(%)	1.70	1.55	1.80	1.89	4.97	5.00	2.99	3.00	4.18
5	Water Yield	(gpt)	4.07	3.71	4.31	4.52	11.92	11.98	7.18	7.18	10.02
6	Oil Yield	(gpt)	17.81	18.64	28.25	28.14	20.27	20.30	13.43	13.36	13.89
7	Oil Gravity	(g/c)	0.92	0.92	0.89	0.89	0.91	0.91	0.94	0.95	0.94
8	Water as % of liquid	(%)	19.95	18.30	14.68	15.32	39.20	39.28	36.11	36.19	43.45
9	Gas % of Gas + Liq.	(%)	22.69	22.93	27.11	29.41	18.40	18.45	29.89	30.34	21.34
OTHER ANALYSES OF RAW SHALE											
10	Total Carbon	(%)	13.30	13.80	17.80	17.60	14.70	15.20	14.00	←	13.90
11	Hydrogen	(%)	1.30	1.30	1.90	1.90	1.80	1.60	1.70	←	1.70
12	Nitrogen	(%)	0.10	0.20	0.30	0.30	0.30	0.30	0.10	←	0.10
13	Mineral Carbon	(%)	4.80	4.70	3.10	3.10	3.40	3.20	0.32	←	0.14
14	RSOC* (by dif.)	(%)	8.50	9.10	14.70	14.50	11.30	12.00	13.68	←	13.76
15	Rock Density	(g/c)	2.31	2.31	2.17	2.17	2.18	2.19	2.27	←	2.23
16	Bulk Density	(g/c)	1.05	←	1.02	←	1.02	←	1.08	←	1.04
17	Void Fraction	(%)	54.55	←	53.00	←	53.21	←	52.42	←	53.36
18	pH		7	←	7	←	7	←	7	←	7
ANALYSIS OF KILN RUN SPENT SHALE											
19	Total Carbon	(%)	7.20	7.50	7.50	7.90	6.60	6.50	8.40	←	8.30
20	Hydrogen	(%)	0.40	0.40	0.40	0.40	0.50	0.40	0.60	←	0.50
21	Nitrogen	(%)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	←	0.10
22	Mineral Carbon	(%)	4.70	5.20	4.10	4.50	3.70	3.50	0.34	←	0.10
23	SSOC* (by dif.)	(%)	2.50	2.30	3.40	3.40	2.90	3.00	8.06	←	8.20
24	Wt. % Pyrolyzed	(%)	11.2	11.2	19.2	18.6	16.2	16.2	11.9	←	12.71
25	RSOC Pyrolyzed	(%)	73.8	77.5	81.3	80.9	78.5	79.0	48.1	←	47.98
ANALYSIS OF KILN RUN ASH											
26	Total Carbon	(%)	5.60	←	4.90	4.90	4.60	←	4.00	←	6.70
27	Hydrogen	(%)	0.30	←	0.20	0.20	0.20	←	0.20	←	0.30
28	Nitrogen	(%)	0.00	←	0.05	0.05	0.00	←	0.05	←	0.10
29	Mineral Carbon	(%)	4.80	←	3.80	←	3.40	←	0.22	←	0.05
30	AOC* (by dif.)	(%)	0.80	←	1.10	←	1.20	←	3.78	←	6.65
31	Burned Wt. Loss	(%)	2.75	←	3.78	←	2.87	←	4.66	←	2.17
32	Burned C Wt. Loss†	(%)	68.88	←	68.87	←	59.81	←	55.29	←	20.66
33	Total RSOC* Reacted	(%)	91.87	←	94.18	←	91.36	←	76.79	←	58.73
34	Min. Process Grade‡	(gpt)	7.90	←	7.90	←	10.40	←	1.20	←	4.60
35	pH		7	←	9	←	11	←	7	←	7

← In absence of data for this duplicate sample, datum to left applies. Duplicate identical data are shown where available, e.g. Parachute #2 Ash.

* RSOC (Raw Shale Organic Carbon or Organic Carbon as % of Raw Shale), SSOC (Spent Shale Organic Carbon), AOC (Ash Organic Carbon).

Line 25 = $100(RSOC - SSOC) / (1 - \text{Line 24}/100) / RSOC$. Line 33, RSOC pyrolyzed + burned = $100(RSOC - AOC) / (1 - \text{Line 31}/100) / RSOC$.

† This is the fraction of carbon in the spent shale that was burned and is an indication of the coke combustion/oxidation efficiency.

‡ Minimum grade that will just provide sufficient process heat from coke combustion based on actual percentages pyrolyzed and burned.

APPENDIX D

EFFECT OF PROCESSING ON PARTICLE SIZE DISTRIBUTION OIL SHALES & RESIDUES OF RETORTED & BURNED OIL SHALES

PARTICLE SIZE	RAW OIL SHALE		RETORTED OIL SHALE		BURNED RESIDUE	
Sieve Opening	Weight		Weight		Weight	
Mesh (mm)	(grams)	(%)	(grams)	(%)	(grams)	(%)
OCCIDENTAL, GREEN RIVER OIL SHALE						
-4+7	2.83	111.29	11.5	36.05	4.1	0.0
-7+14	1.40	514.67	53.3	371.87	42.0	341.63
-14+20	0.85	153.42	15.9	168.49	19.0	152.69
-20+35	0.42	116.11	12.0	134.95	15.2	117.02
-35+60	0.25	47.40	4.9	51.17	5.8	44.16
-60+100	0.15	30.14	3.1	30.79	3.5	31.06
-100	-0.15	0.00	0.0	93.10	10.5	131.24
Total	973.04	1.0	886.42	100.0	817.80	100.0
PARACHUTE, GREEN RIVER OIL SHALE						
-4+7	2.83	259.58	0.3	86.66	11.2	82.64
-7+14	1.40	387.41	0.4	275.38	35.6	269.78
-14+20	0.85	124.15	0.1	108.33	14.0	106.09
-20+35	0.42	103.44	0.1	87.83	11.4	85.29
-35+60	0.25	42.73	0.0	34.31	4.4	36.03
-60+100	0.15	25.60	0.0	20.61	2.7	22.18
-100	-0.15	22.84	0.0	160.46	20.7	151.77
Total	965.76	1.0	773.60	100.0	753.78	100.0
TIPTON, GREEN RIVER OIL SHALE						
-4+7	2.83	85.09	0.1	37.61	0.0	40.58
-7+14	1.40	368.18	0.4	262.33	0.3	226.16
-14+20	0.85	192.05	0.2	161.58	0.2	150.94
-20+35	0.42	161.42	0.2	138.40	0.2	140.54
-35+60	0.25	68.90	0.1	59.88	0.1	55.47
-60+100	0.15	45.68	0.0	44.58	0.1	31.08
-100	-0.15	50.89	0.1	109.11	0.1	135.54
Total	972.22	1.0	813.48	1.1	780.31	103.5
KENTUCKY, EASTERN OIL SHALE						
-4+7	2.83	110.15	10.1	73.23	7.6	90.94
-7+14	1.40	530.46	48.6	457.94	47.5	376.16
-14+20	0.85	200.99	18.4	178.52	18.5	157.25
-20+35	0.42	157.72	14.5	139.95	14.5	115.01
-35+60	0.25	58.93	5.4	52.73	5.5	41.47
-60+100	0.15	27.33	2.5	28.61	3.0	24.42
-100	-0.15	5.51	0.5	32.56	3.4	52.18
Total	1091.09	100.0	963.54	100.0	857.43	100.0
INDIANA, EASTERN OIL SHALE						
-4+7	2.83	0.00	0.0	0.00	0.0	0.87
-7+14	1.40	559.33	56.9	474.15	54.8	335.45
-14+20	0.85	174.62	17.8	154.04	17.8	118.26
-20+35	0.42	139.61	14.2	120.96	14.0	92.46
-35+60	0.25	59.24	6.0	50.26	5.8	37.81
-60+100	0.15	37.79	3.8	32.78	3.8	24.54
-100	-0.15	12.08	1.2	33.55	3.9	25.88
Total	982.67	100.0	865.74	100.0	635.27	100.0

SIZE DISTRIBUTION GRAPHS

APPENDIX E

FISCHER ASSAY ANALYSES OF OIL SHALES; DATA SUPPLIED BY WRI & LLNL WITH OIL SHALE

WRI Sample No.	Oil Yield (gpt)	Oil SpG (gr/cc)	Water Vol. (gpt)	Oil (< 8.341)	Water lb/ton	Gas + Loss	Residue due to Gas + Oil	Ratio of Gas to Gas + Oil
GIROS W-86, Mahogany Lodge, Parachute mbr., Piceance Creek, Exxon Colony Mine								
1	28.3	0.890	3.4	210.0	28.4	79.0	1683	0.273
2	27.6	0.889	4.3	204.7	35.9	79.0	1681	0.278
3	27.5	0.891	3.6	204.4	30.0	79.0	1687	0.279
4	26.4	0.911	4.8	200.6	40.0	94.0	1665	0.319
5	27.9	0.889	3.6	207.0	30.0	76.0	1686	0.269
6	27.9	0.891	4.1	207.3	34.2	82.0	1676	0.283
7	27.9	0.893	4.0	207.8	33.4	94.0	1666	0.311
8	25.9	0.890	4.3	192.2	35.9	89.0	1684	0.316
9	27.9	0.884	4.4	205.6	36.7	94.0	1663	0.314
10	26.2	0.890	5.1	194.5	42.5	82.0	1680	0.297
Average	27.4	0.892	4.2	203.4	34.7	84.8	1677	0.294
StdDev	0.9	0.007	0.5	5.9	4.5	7.2	9	0.020
Eastern Oil Shale E-86, Knierim Quarry, Bullitt County, Kentucky								
1A-1C	14.9	0.974	3.5	120.9	29.2	58.0	1791	0.324
2A-2C	15.0	0.938	3.2	117.2	26.7	67.0	1790	0.364
3A-3C	14.8	0.946	3.3	116.6	27.5	56.0	1799	0.324
4A-4C	14.9	0.944	3.7	117.2	30.9	58.0	1794	0.331
5A-5C	15.1	0.947	2.5	119.1	20.9	69.0	1791	0.367
6A-6C	14.6	0.946	4.7	115.1	39.2	61.0	1785	0.346
7A-7C	14.9	0.943	4.6	117.1	38.4	60.0	1785	0.339
8A-8C	14.9	0.942	4.7	116.9	39.2	58.0	1786	0.332
9A-9C	15.9	0.947	4.6	117.5	38.4	63.0	1781	0.349
10A-10C	15.4	0.942	4.0	124.8	33.4	63.0	1778	0.336
Average	15.7	0.944	2.8	123.5	23.4	62.0	1791	0.334
StdDev	15.1	0.942	4.3	118.5	35.9	55.0	1791	0.317
11A-11C	14.5	0.944	4.7	114.0	39.2	54.0	1793	0.321
12A-12C	14.7	0.944	4.8	115.6	40.1	66.0	1779	0.364
13A-13C	14.7	0.944	3.7	115.5	30.9	60.0	1793	0.342
14A-14C	14.9	0.953	3.3	118.3	27.5	69.0	1786	0.368
15A-15C	14.7	0.947	4.1	115.9	34.2	59.0	1790	0.337
16A-16C	13.5	0.943	5.9	106.0	49.2	56.0	1788	0.346
17A-17C	14.4	0.949	4.2	113.9	35.1	59.0	1792	0.341
18A-18C	14.8	0.940	4.8	115.9	40.1	60.0	1784	0.341
19A-19C	14.9	0.949	4.7	117.8	39.2	66.0	1777	0.359
20A-20C	14.0	0.943	5.9	110.1	49.2	61.0	1779	0.356
Average	14.7	0.946	4.3	116.2	35.9	60.7	1787	0.285
StdDev	0.5	0.007	0.8	3.8	7.1	4.2	6	0.015
LLNL SUPPLIED SAMPLE: From Occidental Oil Co. Mine, Tract C-b, Piceance Creek, Colorado, Green River Oil Shale; Grade: 15 GPT.								
WRI Sample No.	Oil Yield (gpt)	Oil SpG (gr/cc)	Water Vol. (gpt)	Oil (< 8.341)	Water lb/ton	Gas + Loss	Residue due to Gas + Oil	Ratio of Gas to Gas + Oil
Green River Oil Shale W-87, Tipton Member, Sweetwater County, Wyoming								
1	23.3	0.915	7.1	177.7	59.2	46.0	1717	0.21
2	22.8	0.914	7.0	173.7	58.4	47.0	1721	0.21
3	24.4	0.913	6.8	185.6	56.7	31.0	1727	0.14
4	22.7	0.915	7.2	173.2	60.0	51.0	1716	0.23
5	23.0	0.913	7.0	175.1	58.4	47.0	1720	0.21
6	22.4	0.917	7.2	171.2	60.0	52.0	1717	0.23
7	23.2	0.917	7.1	177.5	59.2	61.0	1702	0.26
8	22.7	0.916	7.1	173.4	59.2	54.0	1713	0.24
9	22.1	0.915	7.1	168.7	59.2	52.0	1720	0.24
10	21.0	0.916	7.0	160.8	58.4	50.0	1731	0.24
Average	22.8	0.915	7.1	173.7	58.9	49.1	1718	0.22
StdDev	0.9	0.002	0.1	6.4	1.0	7.7	8	0.03
Eastern Oil Shale E-88, Clark County, Indiana								
8-9	19.1	0.943	2.8	150.2	23.4	57.0	1769	0.28
9-10	17.5	0.946	1.6	138.1	13.3	44.8	1803	0.24
10-11	15.6	0.927	2.9	120.7	24.2	41.6	1813	0.26
11-12	16.8	0.933	1.9	130.7	15.8	42.6	1811	0.25
12-13	16.0	0.925	1.8	123.5	15.0	43.8	1817	0.26
13-14	17.0	0.934	2.5	132.5	20.9	47.6	1800	0.26
14-15	17.7	0.932	2.8	137.6	23.4	59.8	1780	0.30
15-16	16.3	0.927	2.8	126.1	23.4	53.8	1797	0.30
16-17	17.8	0.933	1.9	138.5	15.8	62.8	1783	0.31
17-18	14.7	0.944	2.2	115.8	18.4	61.4	1805	0.35
18-19	13.9	0.942	2.3	109.2	19.2	58.8	1812	0.35
19-20	14.0	0.941	2.0	109.9	16.7	65.0	1808	0.37
20-21	13.9	0.939	2.3	108.9	19.2	57.6	1814	0.35
21-22	13.1	0.925	1.6	101.1	13.3	43.0	1842	0.30
22-23	10.6	0.933	1.3	82.5	10.8	37.4	1870	0.31
23-24	11.6	0.935	1.4	90.4	11.7	37.4	1861	0.29
24-25	13.1	0.925	1.7	101.1	14.2	44.0	1841	0.30
25-26	12.4	0.923	1.4	95.5	11.7	41.2	1852	0.30
26-27	13.3	0.935	1.7	103.8	14.2	54.0	1828	0.34
27-28	14.6	0.925	1.8	112.7	15.0	53.6	1818	0.32
28-29	15.6	0.920	1.4	119.7	11.7	53.8	1815	0.31
29-30	14.1	0.922	1.3	108.4	10.8	52.6	1828	0.33
30-31	15.9	0.931	1.1	123.5	9.2	53.0	1815	0.30
Average	16.9	0.934	2.3	131.4	19.4	51.5	1798	0.28
StdDev	2.1	0.007	0.5	16.6	4.5	8.2	24	0.03

APPENDIX F

THERMOGRAVIMETRIC WEIGHT & TEMPERATURE SUMMARY

TGA Sample Run No.	Run Type	Pan (mg)	Gross Wt (mg)	After TGA (mg)	Net Wt (mg)	Final Wt (mg)	Wt Loss (mg)	Wt Loss (%)	Weight Loss Distributed as				Max Temp (C)	Oxide Exthm Peak (C)	
									Water (%)	Pyrolysis (%)	Oxidation (%)	Calcination (%)			
218	X5	Pyr&Oxida	128.8	239.7	224.9	110.9	96.1	14.8	13.32	0.00	10.88	1.76	0.68	524	7.3
203	P1	Pyr&Oxida	131.4	165.0	158.3	33.6	26.9	6.7	19.85	0.19	15.93	1.99	1.74	526	4.0
223	P3	Pyr&Oxida	131.5	210.5	195.1	79.0	63.6	15.4	19.51	0.72	14.15	3.32	1.32	517 531	1.7
204	T1	Pyr&Oxida	128.7	172.2	164.5	43.5	35.8	7.7	17.64	0.42	14.48	2.23	0.51	521	11.0
205	K1	Pyr&Oxida	128.6	193.7	179.6	65.1	51.0	14.1	21.65	0.50	10.31	9.09	0.96	517	14.0
207	I1	Pyr&Oxida	128.6	194.8	178.5	66.2	49.9	16.4	24.70	0.72	12.60	10.06	1.32	525	10.0
208	X1R	Oxidation	128.6	200.0	197.4	71.3	68.8	2.5	3.53	0.00		2.47	0.26	520	0.5
209	X2R	Oxidation	131.4	214.3	212.4	83.0	81.0	2.0	2.36	0.33		1.84	0.19	518	1.0
210	P1R	Oxidation	128.6	235.2	231.3	106.6	102.7	3.9	3.64	0.31		3.02	0.31	516	3.4
211	P2R	Oxidation	131.3	219.1	215.7	87.9	84.4	3.5	3.96	0.17		3.41	0.38	517	3.4
222	P3R	Oxidation	131.3	282.1	275.7	150.8	144.4	6.4	4.22	0.27		3.50	0.45	531	8.7
212	T1R	Oxidation	128.6	202.0	199.4	73.3	70.8	2.5	3.46	0.28		2.86	0.32	516	2.1
214	T3R	Oxidation	131.4	200.8	198.3	69.4	67.0	2.5	3.57	0.33		2.96	0.28	521	1.9
215	K1R	Oxidation	128.8	210.7	201.4	82.0	72.6	9.3	11.38	0.00		11.07	0.31	520	6.7
219	K2R	Oxidation	131.5	207.9	197.5	76.4	66.0	10.4	13.66	0.00		11.93	1.73	714	18.3
216	I1R	Oxidation	131.4	215.6	207.0	84.3	75.7	8.6	10.20	0.18		9.60	0.42	520	7.8
221	I2R	Oxidation	131.4	225.4	214.3	94.0	82.9	11.1	11.80	0.00		10.44	1.36	715	16.0
238	I1R	StepOxidat	128.65	204.12	195.80	75.5	67.2	8.3	11.02	(Stepwise oxidation)				503	

TGA Weight loss attributed to 4 effects is measured at the following time points:

	For Pyrolysis-Oxidation Runs	For Oxidation Runs
Water:	Start to 120C or Valley between Peaks	Start to Valley between peaks near 120C.
Pyrolysis:	End of H2O Pt to point 8 minutes after temp. reaches 500C.	(Not applicable)
Oxidation:	Start of Air Flow to period 6 minutes after peak.	End of H2O Pt to point 8 minutes after temp. reaches 500C.
Calcination:	End of Pyrolysis to start of oxidation + end of oxidation to run end.	End of oxidation to end of run.

Some mineral calcination may have occurred as a part of some of the other measured peaks. For example, the water peak may have included some anhydrous CO2.

Sample Key. X: Occidental; P: Parachute; T: Tipton; K: Kentucky; I: Indiana; R: Residue (pyrolyzed oil shale)

APPENDIX G

L MINIMUM OIL SHALE GRADES WITH INCOMPLETE COKE RECOVERY				
I Calculations show leanest ore grade that will just provide enough				
N coke with indicated % coke combustion for heat required.				
B	Basis: 1 lb Green River oil shale.	Case A	Case B	Case C Case D
#				
8	RETORTING CONDITIONS	[<GreenRiver>]		[<Eastern OS>]
9	Max. temperature of ash, Tmax (F)	1000	1000	1000 1000
10	Percent of Coke Burned (%)	69	60	55 21
11	Ore grade minimum (gal/ton)	14.07	19.33	2.06 7.79
12	Organic content in ore (%)	8.2	11.2	2.341 8.852
13	Spent shale coke (as % of feed ore)	1.6	2.2	1.2 4.4
14	Mineral or ash in feed (lb)	0.92	0.89	0.98 0.91
16	COKE COMBUSTION HEAT AVAILABLE (Btu)	158	189	90 130
18	ORE PREHEAT & PYROLYSIS DATA (from R.L.Wise' data)			
19	Ore preheat, to 700F (Btu)	175	185	150 162
20	Pyrolysis Heat 700-900F (Btu)	72	79	57 64
21	Total preheat + pyrolysis (Btu)	+ 247	265	207 226
23	ASH HEAT DATA (from lit. values of Cp & Wise' data)			
24	Heat/lb ash from 900 to Tmax (Btu/lb ash)	28	28	28 28
25	Heat total ash from 900F to Tmax.(Btu)	26	25	27 25
26	Eject ash heat @ 250F (Btu)	34	33	36 33
27	Heat available above 250F (Btu)	- 176	170	187 174
28	% of heat recoverable (above 250F)	84%	84%	84% 84%
30	HEAT For 105 % Combustion Air	+ 31	38	18 26
31	Heat Loss (12% of line 28)	+ 30	32	25 27
33	NET HEAT REQ'D AFTER HEAT RECOVERY (Btu)	= 158	189	90 130

Calculations: Ore grade is adjusted for heat balance so heat required equals heat available (lines 16 & 33). Line 33 is sum of values indicated with "+" or "-". Heat from coke combustion & heat recovery provide for heating air, retorting shale & heat loss (line 31).

Assumptions: Coke burns at 14,000 Btu/lb (14000 x line 10 x line 13 = line 16). Green River ore grade gpt = 1.72 x %OM (Organic Matter) & 20% of OM goes to coke; shale preheat, pyrolysis, spent shale & ash heat to 900F calculated on basis of modified R.L. Wise data, USBM RI-7482. Ash heat above 900F based on lit. values for ash c_p (.27 Btu/lb/F in range of 900 to 1000F). Eastern oil shale correlations based on Appendix C analyses: gpt = .88 x OM, 50% of OM goes to coke. Heat loss (line 31) based on information of J. E. Sinor in his Evaluation of this project proposal (see Final Report, Ref. 3). (For correlation data see also LLNL RL-53253 and Fuel, v53, p 16.)

**DATE
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10 / 19 / 93

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