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In Situ Noncombustive Microwave
Processing of Oil Shale

MASTER

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In Situ Noncombustive Microwave
Processing of Oil Shale

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SCOPE OF WORK

1. Using existing microwave equipment obtain shale oil and gas samples and perform a chemical analysis on the liquid and gas products using a microcoulometric approach.

Deliverables: An elemental analysis of the liquid and gas products.

2. Perform the necessary measurements and complete a conceptual energy balance and cost estimate for the microwave retorting process.

Deliverables: Recommendations concerning the commercial feasibility of microwave retorting of oil shale.

Abstract

As specified in D.O.E. contract ET-78-S-01-3280 a unified analytical examination of the products of microwave oil shale has been completed. In addition, for comparison purposes, a sample of subbituminous Colorado coal was included since it was observed that the microwave pyrolysis mechanism for oil shale and coal appear to be similar. Analysis systems have been planned, constructed and placed into operation so as to provide a definitive profile of the composition of gases, oil and water released by the microwave heated oil shale and coal samples. A detailed description of the systems have been given in the January-April progress report. The chemical objectives of this study, presented in this report, were designed to provide accurate and precise data on the nitrogen, sulfur, carbon, hydrogen, and on the water, gases and oil, both from microwave retorting procedures and on parallel Fischer Assay tests. The microwave equipment used in this study consisted of a modified 1300 watt Litton commercial microwave oven. The modifications consisted of extensive reorganization of the microwave generation and delivery systems together with a specially designed, stainless steel, high temperature and pressure retort to contain the large samples. A measuring system for forward, backward and absorbed microwave power was also constructed and was described in the January-April progress report.

Analytical Tests and Results

In a previous National Science Foundation study performed in this laboratory, NSF AER75-17453, it was reported that microwave retorted oil shale produced large quantities of high BTU content gas. This result was partially due to the fact that no dilution occurs with microwave retorting as is the case with many thermal processes. In addition, this earlier study indicated that the analysis of the microwave retorted oil was significantly different from the industry recognized standard - the Fischer Assay. In the data presented in this report, using a modular microcoulometric analysis system, a definitive profile of the composition of the gasses, oil and water, released by the microwave retorted oil shale and coal show that the previous results are confirmed.

Analysis of Gases

A summary of the gaseous output for two shale samples and one coal sample is shown in Table I. It is readily observed that higher grades of shale yield more energy per pound of oil shale processed. This would be expected since the organic content of low grade shale is less than that in higher grade shales. The differences in heat values per cubic foot of gas is also to be expected since the higher grades of shale produce higher quantities of methane. In addition, the lower grades of shale produce more carbon dioxide, again, due to the lower organic content.

TABLE I

Sample:	Shale #1	Shale #2	Coal
Gas, oil/ton	14.2	40	N.A.
Weight of sample:	3.69 lb.	0.44 lb.	0.35 lb.
Gas output	4.2 cu.ft.	1.25 cu.ft.	1.7 cu.ft.
% gas & loss	8.16% ^a	17%	22.1%

Gas Analysis: ^b	Cubic Ft.	Vol. %	Cubic Ft.	Vol. %	Cubic Ft.	Vol. %
CH ₄	0.25	(6.0%)	0.45	(35.9%)	0.54	(31.9%)
CO	0.95	(22.6%)	0.22	(17.7%)	0.45	(26.2%)
CO ₂	1.81	(43.1%)	0.18	(14.5%)	0.11	(6.2%)
H ₂	0.01	(0.24%)	0.19	(15%)	0.15	(9%)
C ₂	0.02	(0.48%)	0.16	(14.5%)	0.18	(10.6%)
C ₃	0.02	(0.48%)	0.04	(3.3%)	0.07	(4.0%)
C ₄	0.23	(5.5%)	0.01	(1.0%)	0.06	(3.6%)
C ₅	0.15	(3.6%)	>0.01	(~0.4%)	0.01	(0.7%)
Heat Value of gas:	500 BTU/Cu.Ft.		650 BTU/Cu.Ft.		866 BTU/Cu.Ft.	
Heat value of gas per pound of shale:	569 BTU/lb.		1847 BTU/lb.		4206 BTU/lb.	

a. By Fischer Assay % gas and loss is 1.4%

b. Method of determination of gas composition was described in previous reports

Analysis of Oils

In table II an analysis of the oils obtained from a typical sample of oil shale is shown. The sample selected is sample No. 1 (14.2 gal./ton), which is described in Table 1. In addition, a comparison with the analysis of the oil by Fischer assay is given. The project laboratory data books contain data on many samples and sample No. 1 is taken as typical.

TABLE II
SHALE SAMPLE NO. 1

Method	Microwave	Fischer Assay (a)
oil recovered	83.2g(5%) ^a	
oil analysis		
%C	78.83%	82.84%
%H	10.70%	11.30%
%N	1.83%	1.94%
%S	0.33%	0.24%
Heat Value of oil:	18,044 BTU/lb.	18,250 BTU/lb
Heat Value of oil per pound of rock	897 BTU/lb.	---

(a) Percent of virgin shale

It should be observed that the elemental analysis of the microwave produced oil differs significantly from the oil produced by Fischer assay. This would indicate that a different pyrolysis mechanism occurs in the case of microwave heating. Another observation is the lower carbon and hydrogen content of the microwave produced oil. These lower values do not change the overall heating value of the gas and oil taken together as compared with thermally produced oil.

Analysis of Recovered Water

The water recovered from shale sample No. 1 was analyzed for the total organic carbon content. In Table III a comparison is given with the analysis for the water recovered by Fischer assay.

TABLE III
SHALE SAMPLE No. I

Method	Microwave	Fischer Assay
Water recovered	equivalent to 2.58 gal/ton	equivalent to 3.9 gal/ton
Total organic carbon in water	3870 ppm	13,160 ppm

In Table III, for shale sample No. 1, a large difference in the organic carbon content in the produced water is recorded. Again, this suggests that a different pyrolysis mechanism of the kerogen occurs with microwave heating, which results in the generation of oil fractions that are less soluble in water than those generated by conventional thermal pyrolysis. In Table II, it was seen that the generation of these less soluble oil fractions is not detrimental to the overall heating value of the oil produced. Another important result from these data to be observed, is that since microwave pyrolysis produces oil fractions with lower water solubility, the potential for introducing carcinogenic organic matter into the local ecosystem is reduced. This should be a consideration in the selection for any pyrolysis process.

Energy Balance Analysis

The process described concerns the recovery of raw shale oil and gas by an in situ microwave heating process. The method makes use of microwave energy to fracture and retort the oil shale. The microwave energy is absorbed principally by the kerogen and the water content of the shale, thus providing a selective heating process, which minimizes the heat energy loss in the spent shale. Microwave retorting does not involve combustion and consequently there are no products of combustion to contaminate the environment. In addition, this approach minimizes the need for water or major mining operations.

Table IV summarizes product properties obtained from a large range of shale qualities, the larger values generally from richer grades.

Table IV
Properties of Microwave Retorted Shale

Liquid Product

Heat of Combustion	16,000 - 18,044 BTU/lb.
Gravity, API	19
Viscosity, SUS 100	50 - 100
Yield, Fischer Assay	60 - 78%

Gaseous Product

Heat of Combustion, net	500 - 744 BTU/SCF
Heat of Combustion, net (CO ₂ and H ₂ S removed)	700 - 902 BTU/SCF
Yield	2 - 3 SCF/lb shale

An example of an energy balance calculation is shown in Table V. An efficiency of 42% is used for a modern steam electric power plant. In addition, a correction is made for the low efficiency of the laboratory microwave unit.

Table V

Laboratory Data Energy Balance

Shale sample 35 gal/ton

<u>Input(per lb.)</u>	<u>Output(per lb.)</u>	
Unregulated System 300 watts @30 min.	Oil	1708 BTU
0.15 KW-hrs	Gas	1642 BTU
		<u>3350 BTU/lb.</u>

$$\begin{aligned}\text{Input Energy} &= (0.15 \text{ KW-hrs})(3413 \text{ BTU/KW-hr})(\text{Eff.} = 1/0.42)(0.45/0.704) \\ &= 779 \text{ BTU/lb.}\end{aligned}$$

$$\text{Energy Balance} = \frac{\text{Output}}{\text{Input}} = \frac{3350}{779} = 4.3$$

A one dimensional model system has shown that non-heating microwave losses can be limited to less than 10 percent of output power with good engineering. Laboratory experiments have been able to redirect up to 99 percent of the power into the shale. Tube efficiencies in available high power microwave generators are currently about 70 percent and in newly developed 100 KW tubes, have reached 80 percent. It has been suggested to use the latent heat capacity of the spent shale together with the shale-derived water to increase pressure for further cracking and increase oil flow. Radiant heat losses would be minimized within a retorting site occurring mainly in the vicinity of the bore hole.

Energy Cost Estimate

An energy cost estimate based on the evaluation of experimental results and data is calculated as follows:

1. Using an average grade of shale (35 gal/ton) or (39.2 gal/metric ton) and the average heat capacity of shale as 0.25 cal/g°C, and an average pyrolysis temperature as 460°C, the energy required per metric ton is: $E_1 = (0.25 \text{ cal/g}^\circ\text{C})(4.185 \text{ Joules/Cal})(10^6 \text{ cal/ton})(460^\circ\text{C})$
 $= 4.8 \times 10^8 \text{ Joules/metric ton.}$

2. Absorbed microwave energy due to selective heating of kerogen and minerals is: Average value 31.2%

$$E_2 = (4.8 \times 10^8 \text{ Joules/mt})(0.312) = 1.5 \times 10^8 \text{ Joules/mt}$$

3. Energy per barrel: (shale grade is 39.2 gal/mt)
(39.2 gal/mt)(0.78 microwave retorting yield)
 $= 30.6 \text{ gal/mt}$

$$\begin{aligned}E_3 &= (4.8 \times 10^8 \text{ Joules/mt})(1 \text{ mt}/30.6 \text{ gal})(42 \text{ gal/bbl}) \\ &= 6.59 \times 10^8 \text{ Joules/bbl}\end{aligned}$$

4. Electric energy per barrel:

$$E_4 = (6.59 \times 10^8 \text{ Joules/mt}) (1 \text{ KW h}/3.6 \times 10^6 \text{ Joules}) \\ = 183 \text{ KWh/bbl.}$$

5. Efficiency of microwave source:

Power supply efficiency = 88%

100 KW microwave generator = 80%

88% X 80% = 70.4% conversion efficiency

6. Input energy (power line):

Without heat energy recovery and including an auxiliary energy estimate of 13%

$$E_6 = (183 \text{ KWh/bbl}) (1/0.704) (1.13) = 294 \text{ KWh/bbl}$$

7. Cost of electric power: Using Colorado Ute R.E.A. cost figures:

Megawatt bulk energy with a 24 hour load factor:

$$(294 \text{ KWh/bbl}) (0.012 \text{ \$/KWh}) = \$3.76/\text{bbl}$$

8. Estimate of replacement and capital costs:

Capital, replacement, labor, maintenance

Cost. = \$5.57/bbl

9. Calculated value of high BTU gas:

Gas output: $(2.5 \text{ SCF/lb}) (2000 \text{ lbs/ton}) = 5000 \text{ SCF/ton}$

Gas value: $(\text{CO}_2, \text{H}_2\text{S removed}) = 902 \text{ BTU/SCF}$

Natural gas equivalent: $(902/1000) (5000) = 4510 \text{ SCF/ton}$
 $= 5412 \text{ SCF/bbl}$

Value (wholesale): $(5412) (0.90 \text{ \$/1000 SCF}) = \$4.87/\text{bbl}$

The above calculated results are tabulated as follows:

Cost of electric energy:	\$3.76 per barrel
Capital cost:	\$5.57 per barrel
Market value of gas:	\$4.87 per barrel equiv.
Net cost per barrel:	$\$3.76 + \$5.57 - \$4.87 = \4.46

It should be emphasized that these calculations are based on bench scale laboratory data. Scale up to prototype and full scale will introduce factors and costs which are impossible to predict at this stage of development.

Overall capital costs are estimated using the laboratory-scale work completed to date. The estimates use published analysis of TOSCO and Shell Oil for reference. Most impressive is the lower capital investment the ability to increase capacity in a modular manner. Processing equipment will be that which is currently available to the chemical and microwave engineering industry. Operating costs include predictable drilling and power estimates, and the costs of operating chemical processing equipment above ground. Because of the excellent flow properties of the oil, on site refining could be accomplished, but since the liquid fuel is of pipeline quality and of good stability, economics initially would dictate transportation. The gaseous product, once the hydrogen sulfide and carbon dioxide are chemically removed, rivals natural gas in BTU output and would be transportable, the gas could also supply a large portion of the electric power used by the microwave generators.

The microwave insitu process is environmentally desirable compared with other oil shale processes for several reasons. Large quantities of spent shale are not disposed of on the surface and water consumption is limited to processing of the shale oil on the surface. Blasting with explosives for rubblization is unnecessary. Because of the reductive atmosphere in the retorting zone, nitrogen oxides emissions are expected to be lower than that of other processes using combustion. Capital and operating cost calculations indicate that the microwave retorting process should be tested on a larger scale.

Research Summary

Early experimentation showed that the shale strata, devoid of organic matter, had low power absorption properties and a selective and sequential heating situation was demonstrated. That is, the initial fixed water instantaneously heated and expanded causing fracturing of the shale. This was followed by kerogen pyrolysis and lastly by the absorption of power by the shale. This selective microwave interaction indicated lower power requirements than a strictly thermal process. After the water vaporization phase, sulphurous gas appeared followed by oil vapor and mist, which continued to completion. The spent shale remained solid,

but with much less structural integrity and with extensive fracturing generally along the bedding plane. This greatly increasing the shale porosity. Since gas evolution was quite copious, it was assumed that it contained a large proportion of the overall heating value of the product. This was later confirmed. Also, because of the closed nature of the system, no dilution of the gas occurred and the calorific heating value was found to be much higher than most direct heating processes.

Table VI lists results of microwave retorted Green River oil shale (35 gallon per ton). These experiments indicated a need for comparative studies with thermally produced liquid and gaseous products. Flow property indicators (API gravity, pour point), showed conflicting trends. The gas output was very high.

Table VI

Microwave Retorted Green River Oil Shale

Gas and Losses	21.0%
Carbon in Semicoke	4.5% (percent of spent shale weight)
Oil Yield	71.0% (percent of Fisher Assay)
Heat of Combustion	17,394 BTU/lb
API Gravity (Pour Pt 30°F)	18.1
Nitrogen	1.9%
Sulfur	0.93%
Conradson Coke	5.5%
Ash	0.3%

Coking has been described as the main degradation mechanism of shale oil by thermal heating. Microwave retorting produces low residual carbon, therefore cracking reactions would more easily describe the increased gas production by microwave retorting. The effective gas and oil production rate in microwave retorting is so rapid that cracking reactions must occur inside the shale as soon as oil liquid is produced (microwave interaction is greatly decreased in gas phase reactions).

Results from a series of experiments performed under maximal energy absorption conditions are shown in Table VII. These samples were subjected to a microwave field until gas and vapor evolution returned to near background. These conditions are not those of maximal efficiency either

in power used or in yield obtained, but do show a direct comparison to a thermal retorting system with the modified Fischer assay as an "indirect process" reference.

Table VII

Microwave Retorted Shale Oil Compared with Fischer Assay Oil

Number of Experiments	Grade (gal/ton)	<u>Fischer Assay Oil</u>		<u>Microwave Oil</u>	
		Specific Gravity	Pour Point, °F	Specific Gravity	Pour Point, °F
3	68.8	0.896	53	0.956	45
2	40.6	0.917	69	0.934	< 10
2	23.0	0.926	53	0.937	19
2	12.5	0.950	60	0.940	37

The microwave run was complete within 30 minutes since dependence on heat transfer as in the thermal retort is unnecessary. In comparing some characteristics of the oils obtained, significant differences in the overall specific gravity and in the pour points were observed. The Fischer assay specific gravity decrease correlated well with increasing yield, as is often the case in the literature. In all cases the specific gravity of the microwaved oil is higher than the Fischer assay oil, this held true for every sample tested. Yet the microwave oils show excellent flow properties which were later confirmed by kinematic viscosity measurements.

It has been noted that shale oil properties can vary with the percentage yield of a thermal process. The percentage of oil recovery as compared to the Fischer assay is presented in Table VIII.

Table VIII

Residues from Microwave and Fischer Assay Processed Shales

Grade (gal/ton) Ave.	<u>Fischer Assay</u>		<u>Microwave</u>	
	Spent shale	Ash	Spent Shale	Ash
	(% of initial sample weight)		(% of initial sample weight)	
68.8	67.8	60.8	60.2	57.9
40.6	79.3	75.8	65.8	62.8
23.0	87.8	85.5	76.5	75.6
12.5	91.6	89.5	75.3	74.9

Table VIII shows more characteristics of the retorting runs of Table VII. The data indicate a decrease in the amount of non-retorted volatiles remaining in the high yield shales after microwave retorting. In the lower grades, when comparing ash figures for the two models, the microwave interaction with the shale residue has volatilized some of the spent shale not normally volatilized during low temperature ashing. This interaction can be verified in Table IX by examining the gas percentages of the two processes. The enormous percentage of gas evolved cannot be accounted for by just the decrease in the yield of oil or by even the total loss of organic carbon of oil and coke.

Table IX

Yields of Oil and Gaseous Products

Grade	Fischer Assay		Microwave		
	Oil, %	Gas & Losses, %	Oil, % (Recovery%)	Gas & Losses, %	
68.8	25.7	5.3	17.2	(67)	20.9
40.6	15.5	4.1	8.1	(52)	17.6
23.0	8.9	2.6	6.4	(72)	19.6
12.5	5.0	2.0	3.4	(68)	18.9

The release of fixed water together with the decomposition of kerogen and oil degradation are apparent reactions occurring during the generation of products by microwave interaction. The Molar composition of the gas Table X is examined in reference to the remaining chemical reactions in Table IX. The results would coincide with a mechanism of increasing tendency for bond rupture in areas of permanent dipoles of the kerogen macrostructure.

Table X

Gaseous Products Composition from Microwave Processed Oil Shale

Composition (Mole %)	
(sample 35 gal/ton)	
Carbon Monoxide	17.7%
Carbon Dioxide	14.5
Hydrogen	15
Hydrogen Sulfide	3.0
Methane	35.9
Ethanes	12.4
Propanes	3.3
Butanes	1.0
Pentanes	0.2
Hexanes +	0.2

In these studies, the possibility exists that the kinetics of gas formation have been modified or require a different mechanism of localized interaction within the macrostructure. The larger, more amorphous the structure, the greater the opportunity for produce ratio inversion by the localized "high temperature" power input to specific bond types.