

WALL ET

DAMRAUER R

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*CHEMICAL AND PHYSICAL PROPERTIES OF SHALE OIL
FROM MICROWAVE HEATING

E. T. Wall, R. Damrauer, W. Lutz, R. Bies, and M. Cranney
University of Colorado at Denver

ABSTRACT

Shale oil and a fuel gas have been produced by microwave heating oil shale in a standard microwave oven in conjunction with experimentation in development of an insitu microwave retorting process.

Various grades of oil shale have been subjected to high microwave fields and the derived oil has been submitted to various testing procedures. Among these are specific gravity, pour point, % H₂O, % ash, % gas and losses, % coke, % of Fisher assay, and others including gas composition. These data are compared with parallel data obtained on Fisher assay oil. Important differences in oil flow properties and gas composition are discussed in view of microwave interactive theory.

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Oil shale represents an enormous reserve of fossil fuel for domestic and foreign needs (1, 2). Shale oil recovery processes can be divided into direct and indirect heating processes (2). In direct heating, some of the products or some other fuel is combusted to raise the oil shale to the necessary temperature for release of gas and oil, while an indirect process transfers heat from an outside source. Although high yields have been demonstrated in some indirect procedures (3), the application to insitu retorting has been limited. Direct processes developed for insitu recovery of shale oil have not demonstrated sufficient control of the underground combustion for reliable operation.

Electromagnetic radiation in the microwave frequency spectrum is absorbed most strongly by molecules with permanent dipole moments (4). The relaxation phenomenon of this absorbed power manifests itself in a heat like reaction. The University of Colorado Oil Shale Project has studied the degradation of the liquid-fuel precursor, kerogen, by microwave interaction. Kerogen is a moderately strong absorber of this radiation due to its large percentage of polarized bonds and entrapped polar molecules (5). Microwave retorting represents a controllable underground application of energy without combustion.

It is well known that important differences do occur with different methods of thermal retorting and microwave interactive theory indicates even greater differences may be possible. We examined the products of this novel retorting system using product quality as feedback control and to gain some insight into the basic microwave interaction with fuel precursors.

EXPERIMENTAL

A commercial microwave unit, rated at 2450 MHz and 650 watts, was modified to fit beaker shaped quartz retort of approximately 500 ml capacity in which the oil shale was placed. Much effort was expended with this original design in obtaining materials, both of low-loss, and high thermal stability. The apparatus was required to be gas tight. Oil shale of a block configuration with sides parallel to the bedding plane was halved with one piece retorted and the other ground for Fisher analysis of maximal oil content. Sharp projections of rock were removed and the retort was centered in the cavity and sealed. The unit was activated and the oil and gas produced were fed through glass tubing to a series of condensers, a mercury manostat, stainless steel bellows diaphragm pump, a gas test meter, and various gas collection apparatus (see Figure 1). The experiment can be varied in the manner of collection of products, atmosphere in the retort, sample size, and kerogen/water content.

The other half of the rock was ground to pass through an 8 mesh screen, rifled, and a sample taken for a modified Fisher assay, using a mercury manostat instead of solenoids (6). Gas collection was either metered or collected over water. The apparatus was obtained from the Colorado School of Mines Research Institute with the temperature program controlled manually with a chromel-alumel thermocouple readout. The signal from the thermocouple was monitored by a Radiometer pH/mv meter and outputed to a calibrated laboratory recorder. After a period of time, depending on sample load, water vapor condenses in the first traps, accompanied by major cracks appearing parallel to the bedding plane. After the majority of the water vapor condenses, sulphurous gas appears, followed by oil vapor and mist, and continuing to completion. The coke remains solid, but with much less structural integrity and with serious fracturing along planes parallel to the bedding plane, together with many small cracks greatly increasing the shale porosity.

The literature has virtually no references for using a commercial microwave oven unit for high temperature applications on a closed system. Each observation and parameter changed gave important data and direction in designing a possible microwave interactive process. Quartz was required because of its lower microwave energy absorption (7), and low reflectivity, a quality not well understood, but well documented in our experiments. A newer apparatus, essentially a new cavity, with greater loading and better reproducibility is nearing completion. Gas output was copious often overloading condensing and separating systems. Also, loading of the solid shale indicated a minimum weight below which coupling with the microwave energy was ineffective. Mist formation exceeds the nominal 3-5% reported in the literature for many processes (8). Nucleation methods have not as yet been attempted.

The Bureau of Mines crude oil analysis (9) was used initially to describe the overall quality of the product. The gaseous product was examined using a Perkin Elmer 3920B programmed temperature chromatograph. 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 system, no dilution of the gas occurred and the calorific heating value should be higher than most direct heating processes. Oxygen and nitrogen content were used as a leakage indicator and the gas outputs were adjusted as to volume and energy content.

Crude absorption measurements were made by measuring the temperature rise of known quantities of water and shale in a standard microwave oven. Although by no means an exhaustive study, this method allowed as to confirm the level of power consumption and its variation with kerogen content.

RESULTS AND DISCUSSION

Microwave Power

Microwave heating has enjoyed renewed interest with the development of ovens for the home and high power, high efficiency, industrial equipment. Microwave interaction has long been used to probe structural details of polymers (10) and rotational/vibrational spectra of small molecules. Higher power applications have become more prominent.

In considering the mechanism of interaction of microwave energy and materials a simplified model of a capacitor with the material between charged plates can illustrate the more important aspects of heating (4). The ability of the material to maintain the charge separation, that is, resist current flow is closely related to the inverse of the dielectric constant (ϵ'). When materials are subjected to the electric field between the plates, those with permanent dipoles (polar molecules) will orient their partial positive charges toward the negative capacitor plate. This phenomenon is known as polarization.

Polarization can be classified as electronic (electron cloud distortion), atomic, molecular, ionic and crystalline. The point of maximum polarization in a system would occur when all dipoles reacted to the applied field and aligned. This is difficult to obtain even in a static situation. In an alternating field situation, the dielectric remains the same or decreases as the frequency increases past the microwave region (11). In a microwave region, attainment of equilibrium is more difficult and there is an observable lag in the dipole orientation which is commonly called relaxation. The polarization then acquires a component out of phase with the field thermal dissipation of some of the energy of the field. This dissipation and its relation to the normal charging current can be related by

$$\tan \delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\epsilon''}{\epsilon'} \quad (1)$$

where ϵ' is the measured dielectric constant of the material and ϵ'' is its loss factor. As the frequency approaches zero, ϵ'' approaches zero and ϵ' approaches the static dielectric constant (12). At very high frequencies most of the polarization disappears. Small molecular polarizations in a low viscosity medium would give a maximum near the microwave frequencies; large molecules with restricted orientation freedom, would have maxima at frequencies lower than

microwave. However, true resonance effects are not seen in impure or mixed materials. The behavior of the dielectric constant and loss factor are often considered separately for a given material because the only loss constant usually changes dramatically in the microwave region.

$$\epsilon'' = \epsilon' \tan \delta \quad (2)$$

Hence the $\tan \delta$ can approximate the loss behavior of similar materials (4, 13).

Microwave heating has been called volume heating because of its often independence of thermal conduction. Penetration is inversely proportional to frequency and will be greatest with those materials of low loss (e.g. saturated hydrocarbons, some ceramics, glasses, etc.). Radiated heat from the surfaces of materials heated in microwave cavities can reach high internal temperatures. Low thermal conductivity samples can retain heat build-up until increased rotational freedom can be obtained and then absorb power at a more rapid rate. Some materials heat so slowly by thermal conduction that either size reduction or volume heating would be practical (14). Application to the fracturing of concrete, using broadcast microwave power takes advantage of the low thermal conductivity to concentrate heating interaction (4).

High polymers always have atomic and electronic polarization contributing to the dielectric constant. In heterogeneous materials, an additional type of polarization arises from an accumulation of charge between phases with a corresponding loss. High polymers containing polar groups can show orientation polarization due to chance in orientation of molecular segments, in an externally applied field, without changing the entire molecular orientation (10). Crosslinking of the polymer segments can reduce this freedom considerably. Pure rubbers is a hydrocarbon with little polarity. When it is vulcanized, the reaction with sulfur gives crosslinking with a corresponding increase in dielectric constant due to polar carbon-sulfur bonds. However, as crosslinking increases, the rotational freedom is restricted and the dielectric constant decreases. Here also, interfacial polarization contributes to the overall loss (10).

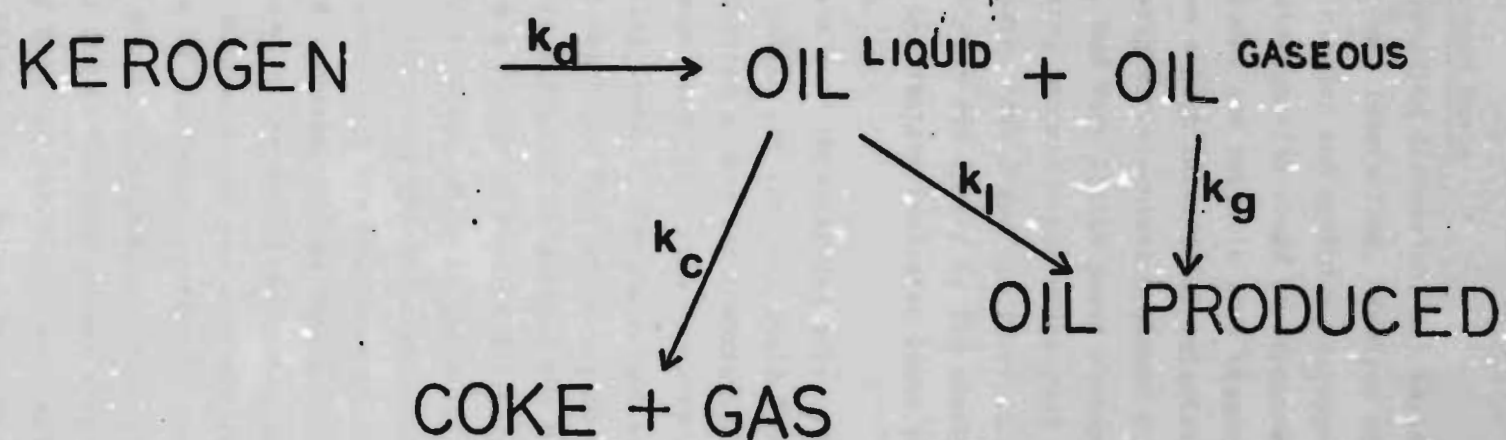


Figure 2. Simplified Mechanism for Oil Production (15)

Oil From Microwaved Shale

From the preceding discussion, oil shale would offer an interesting substrate for microwave power interaction. Kerogen is chemically composed of many segments with permanent dipoles and contains entrapped polar compounds (5, 15). Although a solid, its heterogeneity would be expected to and did display a liquid-like dielectric constant and suitable loss tangent. Also its layered structure in the shale would have a high interfacial polarization contributing to power absorption. Early experimentation showed that the rock strata, devoid of organic matter, had very little power absorption properties (14) and a sequential heating situation was envisioned and demonstrated. That is, the initial fixed water heated and the fracturing of the shale was followed by kerogen pyrolysis and lastly by the absorption of power by the spent ore. This selective interaction indicated lower power requirements than a strictly thermal process.

Table I lists some physical characteristics of shale oil derived from microwaved (35 gallon per ton) oil shale from Rifle, Colorado. These initial 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. Figure 2 shows the most documented reactions (15) occurring in kerogen degradation in thermal processes. It is difficult to account for both low coke and high gas output.

Results from a series of experiments performed under maximal energy absorption conditions are shown in Table II. 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. The microwave run was complete within 30 minutes since dependence on heat transfer as in the thermal retort is unnecessary. 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. The trend for greatest pour point depression seems to be in the area of middle grade of Colorado oil shale.

Table III shows some more characteristics of the retorting runs of Table II. 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, it is apparent, when comparing ash figures for the two models, that the microwave interaction with the shale residue has volatilized some of the rock matrix, or at least modified it in some way as to allow volatilization at 750°F in an oxidizing atmosphere. This interaction can be verified in Table IV in 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.

Averaged overall properties of the crude oil obtained by microwave interaction are summarized in Table V. Although these published figures are not the best for some of the processes listed (2), they are presented for an approximate comparison. It is obvious from these data that microwave produced oil is a suitable liquid fuel precursor although differing from that produced from a variety of thermal processes. The recoveries from this prototype multimode cavity retorting system are very promising.

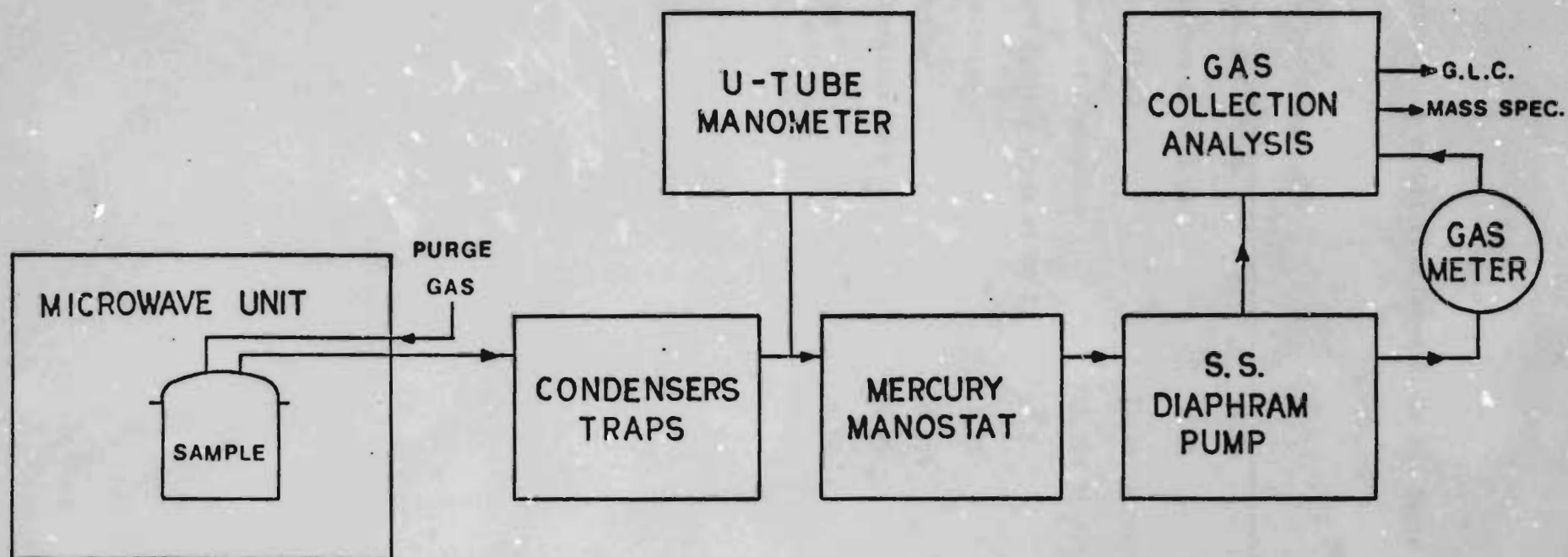


Figure 1. Schematic Representation of Microwave Retorting Operation

Table I Characteristics of Oil from Green River Oil Shale by Microwave Heating

Gas and Losses	21.0%
Carbon in Semicoke	4.5%
Oil Yield	71.0% (percent of Fisher Assay)
Heat of Combustion	16.744 Btu/lb
API Gravity (Pour Pt 30°F)	17.2
Nitrogen	1.9%
Sulfur	0.93%
Conradson Coke	5.5%
Ash	0.3%

Table II

Comparison of the Characteristics of Microwave produced oil and oil from the modified Fischer Assay of divided oil shale samples.

Number of Experiments	Grade (gal/ton)	Fischer Assay Oil		Microwave Oil	
		Specific Gravity	Pour Point, °F	Specific Gravity	Pour Point, °F
3	68.8	0.896	53	0.956	45
3	40.0	0.916	69	0.933	6
2	23.0	0.926	53	0.937	19
2	12.5	0.940	60	0.940	37

Table III

Comparison of Residues from Microwave and Fischer Assay Processed Shales

Grade (gal/ton)	Fischer Assay		Microwave	
	Shale coke, %	Ash, %	Shale coke, %	Ash, %
68.8	67.8	55.6	60.8	56.7
40.0	80.9	65.7	72.8	64.8
23.0	87.8	85.5	72.8	66.2
12.5	91.6	89.5	75.3	74.9

Table IV
Yields of Oil and Gaseous Products

Grade	Recovery%	Fischer Assay		Microwave	
		Oil, %	Gas & Losses, %	Oil, %	Gas & Losses
68.8	67	25.7	5.3	17.2	20.9
40.0	51	15.3	4.1	7.8	18.0
23.0	72	8.9	2.6	6.4	19.6
12.5	68	5.0	2.0	3.4	18.9

Table V

Properties of Crude Shale Oils from Microwave Process and ex situ Processes

Process	Microwave	NTU ^a	Gas ^a Combustion	TOSCO II ^a	Union ^a
Gravity, API	19	25.2	19.7	28	20.7
Sulfur, %	0.85	0.76	0.74	0.8	0.77
Nitrogen, %	1.80	1.77	2.18	1.70	2.01
Pour Point, °F	35	70	80	75	90
Viscosity, SUS 100	60	79	256	120	223
% of Fischer Assay	70	62	85	106	86

^a Data from Reference (2).

Table VI

CHEMICAL REACTIONS IN SHALE PARTICLES (15)

DECOMPOSITION OF KEROGEN

DECOMPOSITION OF CARBONATE MINERALS

REACTION OF CARBON WITH CO_2 REACTION OF CARBON WITH O_2

THERMAL DEGRADATION OF OIL

RELEASE OF FIXED WATER

Table VII

Gaseous Products Composition from Microwaved Oil Shale

Gaseous Product

Heat of Combustion, net 500 - 700 BTU/SCF

Heat of Combustion, net 700 - 900 BTU/SCF
(CO₂ and H₂S removed)Yield 2 - 3 SCF/lb
shaleComposition (Mole %)
(sample 35 gal/ton)

Carbon Monoxide	17.7%	Heating Value (calculated) approx. 744 BTU/ft ³ CO ₂ H ₂ S 902 BTU/ft ³ removed
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	

Gas Analysis

The gas output from initial experimentation was copious. Table VI lists chemical reactions possible with thermal processes in shale particles. The release of fixed water together with the decomposition of kerogen and oil degradation are apparent reaction occurring during the generation of products by microwave interaction with the shale blocks. The Molar composition of the gas (see Table VII) is examined in reference to the remaining chemical reactions in Table VI. The results would coincide with a mechanism of increasing tendency for bond rupture in areas of permanent dipoles of the kerogen macrostructure.

- A. High CO. The retorting had been performed in a closed system initially flushed with nitrogen. Since the CO content of the gas remained fairly constant through out the retorting process, high temperature (i.e. high temperature throughout the shale) reactions are not likely, for example $\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$

An altered mechanism of pyrolysis in the presence of the intense microwave field is suspected for those compounds with a tendency to coke producing CO and liquid fuels. Low coke values in the solid residue might add further evidence.

- B. Moderate to low CO₂. The value in the table represented the overall percentage composition. Sequential analysis showed a fairly linear increase in the CO₂ content. Since low temperature ashing studies did show some degradation of the carbonate matrix under intensive microwave heating for prolonged periods, it is surprising that this value was not higher. Reports in the literature on gas composition from TOSCO-modified Fischer Assay apparatus suggested that half the CO₂ in the product gas was of inorganic origin (6). This would leave very little CO₂ gas to be produced by pyrolysis indicating possibly altered kinetics of degradation.
- C. Low Hydrogen Levels. These levels would be consistent with the rapid degradation of the kerogen and the low coking levels observed. The possibility exists for active reforming of compounds with hydrogen at the reaction sites.
- D. High Methane Content. High methane content together with the high CO levels indicate a predominantly gasification process and fits a hydrogen conserving interaction.

E. Low Pentane + Fractions. During the product collection, all gases and vapors were required to flow past silanized glass wool for mist reduction. Also extensive dry ice cooling was used. These factors may account for the lower values seen. Debutylization of the liquid product was not performed and these dissolved gases were probably lost in the water separation procedure. These losses would further upgrade the BTU output of the gas.

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

Conclusions

The unique nature of microwave power as applied through matter to reactant absorbers has increased the scope of our investigations to encompass more basic studies of the chemical-microwave interaction. The matrix component (shale, sand, etc.) of this interaction is being examined presently by electrical experiments and calculations (dielectric components, permittivity, thermal capacity and conduction).

The data presented suggests the possibility of selecting feedstock or raw materials for a specific product mix. The high quality of both the liquid and gaseous products indicates the advantages of indirect reactions using applied microwave power.

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