

Microwave Heating of New Brunswick Oil Shale



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ABSTRACT

Microwave energy is used to heat New Brunswick oil shale to pyrolysis temperatures. Chromatographic analysis of the liberated gases revealed the presence of carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetylene. Average oil yield was 90.6% of the Fischer assay. Net energy ratio (energy out/energy in) of 3 is predicted for a moderate grade shale of 22 U.S. gal/ton.

INTRODUCTION

Research into the development of a commercially viable shale oil recovery process has been in progress for two decades. Studies have been made into the feasibility of both in-situ and surface retorting techniques. The latter produce enormous quantities of spent shale and the mining of the material is expensive. The development of in-situ methods would eliminate these problems.

Bridges et al. [2, 5] have carried out theoretical and experimental studies on RF dielectric heating of both eastern and western U.S. shales. Net energy recoveries (NER) of 3 to 5 have been predicted and 90% of the Fischer assay oil content has been recovered in laboratory scale studies. These workers [3] have conducted similar investigations into RF heating of Utah tar sands with 85% of the bitumen extracted and net energy recoveries of 4 to 10 predicted.

Athabasca tar sand containing 14% bitumen was studied by Bosisio et al. [1], with the result that microwave heating produced a crude oil whose average molecular weight was lower than the original bitumen, thus eliminating the first refining step. The microwave crude oil was like natural or synthetic crude oil. Gaseous by-products were produced in small amounts. Up to 86% of the bitumen was extracted, an improvement over the 70% limit on conventional techniques. The waste was virtually pure sand which poses no environmental hazard. The process has potential for in-situ distillation which removes the need to handle and transport large amounts of material.

This work investigates the use of microwave energy in recovering oil from the Albert oil shale formation in southeastern New Brunswick. A prototype reactor was constructed to enable heating of a small oil shale sample. The reactor was equipped with a sampling valve and gas chromatograph to permit analysis of the gases liberated during the heating process. The experiment is very similar to that performed by Bosisio et al. [1] on the Athabasca tar sands.

EXPERIMENTAL PROCEDURES

The microwave heating and gas analysis apparatus is shown in Fig. 1. A 20-mm diameter quartz tube, containing a solid oil shale sample, was inserted into a test tube applicator (20 mm in diameter), the axis of the tube in alignment with the electric field in the center of a section of WR284 waveguide. The waveguide delivered 100 W forward power at 2450 MHz to the applicator which was followed by a matched termination. No attempt was made to measure the power absorbed by the sample, but this could be determined by monitoring the power delivered to the termination also. Each sample tested was a rectangular block 10 × 10 × 23 mm. A helium flowrate of 600 ml/minute was measured by a rotameter. The helium was used to flush the system prior to application of power. The heating process was timed over a total duration of approximately 16 minutes and a series of 5 to 10 gas samples were introduced into a gas chromatograph. In this manner the amount of gas extracted was determined as a function of time. By weighing the sample after completion of the test the total amount of bitumen extracted also could be determined.

In a second test, the quantity of extracted bitumen versus time was determined by weighing a sample at periodic intervals over a total heating time of 20 minutes. Both experiments were repeated for several samples with different oil contents and physical properties.

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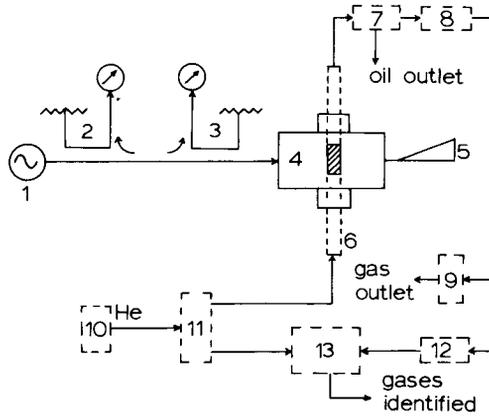


Figure 1 Experimental apparatus; — microwave circuit, --- reactor circuit.

- | | | | |
|-----|--|----|---|
| 1 | Microwave power supply,
0 to 2.5-kW, 2.45-GHz
Crydry I - 2LC | 8 | Glass wool filter |
| 2,3 | Reflected and forward
power meters | 9 | Pressure release valve |
| 4 | WR284 waveguide
test-tube applicator | 10 | Helium gas bottle |
| 5 | Termination | 11 | Rotameter tube bank |
| 6 | Quartz reactor tube
and sample holder | 12 | Gas sampling valve
with 2-cc sample loop |
| 7 | Cold trap | 13 | Gas chromatograph,
GlowMac series 550
thermal conductivity detector |

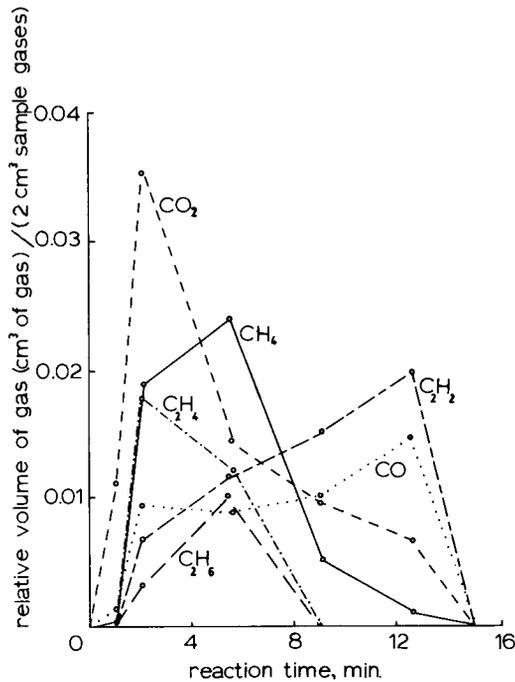


Figure 2 Relative concentration of extracted gases, sample A3

Table 1 Quantity of gases recovered for various samples

Sample	A1	A2	A3	A6	A7	A10
Weight (g)	2.0963	5.3844	4.2316	4.8083	3.6172	3.8435
Heating time (min)	15.00	14.50	15.08	17.50	16.50	16.00
Gas	Volume (cm ³)	Weight (mg)	Volume (cm ³)	Weight (mg)	Volume (cm ³)	Weight (mg)
CO	21.89	27.36	40.12	50.15	66.83	83.54
CO ₂	72.76	143.8	58.58	115.8	65.08	128.6
CH ₄	25.86	18.54	44.14	31.64	26.10	18.70
C ₂ H ₂	—	—	50.10	58.66	1.77	2.08
C ₂ H ₄	11.82	16.04	25.21	34.20	3.75	5.08
C ₂ H ₆	5.75	7.27	12.87	16.27	2.34	2.95
Total	138.1	213.0	231.0	306.7	165.9	240.9
				138.0	161.4	173.8
				91.32	514.4	709.1

Table 2 Comparison of microwave retort (M.R.) with Fischer assay (F.A.)

Sample		A1	A2	A3	A7	A10
Total weight	F.A.	26.0	6.0	13.0	13.0	26.0
loss (%)	M.R.	31.54	6.02	16.06	16.32	38.63
Oil yield	F.A.	20.4	4.3	8.2	7.5	22.4
(%)	M.R.	19.28	3.98	7.32	6.56	19.25
Gas yield	F.A.	3.05	1.3	0.64	2.1	2.1
(%)	M.R.	10.16	1.46	7.25	6.66	18.45
Water yield	F.A.	2.1	0.4	3.1	3.4	1.4
(%) oven dried		2.1	0.58	1.49	2.85	0.93
Oil yield ratio		0.945	0.926	0.893	0.908	0.859
M.R./F.A.						
Gas yield ratio		2.90	1.12	11.33	3.17	8.79
M.R./F.A.						
Oil yield (F.A.)		54.3	12.0	22.2	20.4	61.5
(U.S. gal/ton)						

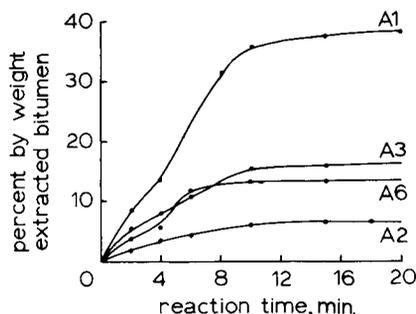


Figure 3 Extracted bitumen vs reaction time

As a basis of comparison a Fischer assay was performed on each sample. This is a standard test for oil shale whereby a 100-g finely crushed sample is brought to 500°C at a fixed heating rate, held at 500°C for a set period of time and the evolved gases condensed. The results of the microwave heating experiment were compared with those obtained from the Fischer assay which employs conventional heating.

RESULTS AND OBSERVATIONS

Six different samples were chosen for microwave heating and gas chromatographic analysis. Two samples, A1 and A2, are Colorado shales, three others, A3, A6, and A7, are from a surface outcrop of the Albert formation, while sample A10 is a drill core also from the Albert formation. Physical and dielectric properties of these and other samples are given by Briggs et al. [4] in a companion paper. Sample designation is consistent with that work.

A typical result of the gas chromatographic analysis for sample A3 is shown in Fig. 2. The graph gives an indication of how the volume of each gas produced varied over the life of the reaction process. Methane (CH_4) shows the most consistent behaviour from sample to sample. In all cases the amount of methane produced increases rapidly for the first two to eight minutes of the reaction time. Once the volume reaches a maximum, it then drops off quickly. Acetylene (C_2H_2) exhibits the same type of behaviour when present, although the time at which it reaches a maximum varies substantially and it is not found over the entire reaction period. The profile of the volume of carbon dioxide (CO_2) is very inconsistent. In samples A6 and A7 it behaves much like methane, increasing in volume rapidly. In samples A2 and A1 its profile resembles that of carbon monoxide (CO), reaching a maximum very slowly and then tailing off to zero. The volume profile of carbon monoxide is very different from those of all other gases. Its volume increases very slowly, reaching a maximum only during the latter stages of the reaction. This would seem to indicate that carbon monoxide is formed in greater quantities only

Table 3 Energy output of raw shale, 1 kg sample A3

Product	Weight (kg)	Heat value	
		Weight (MJ/kg)	(MJ)
CO	0.01185	10.10	0.120
CO ₂	0.02737	0	0
CH ₄	0.00748	55.54	0.415
C ₂ H ₂	0.01386	48.50	0.672
C ₂ H ₄	0.00808	50.36	0.407
C ₂ H ₆	0.00384	51.96	0.200
Gas	0.0725		1.814
H ₂ O	0.0149	0	0
Oil	0.0732	41.77	3.058
Total	0.1606		4.872
Spent shale	0.8394	0.487	0.409

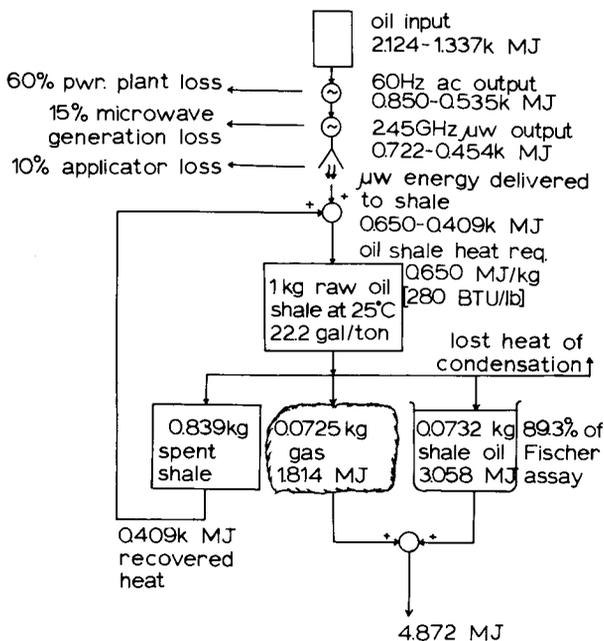


Figure 4 Energy flow diagram

when not enough oxygen is present to enable the complete oxidation of the hydrocarbons to carbon dioxide. The two other gases present, ethylene (C₂H₄) and ethane (C₂H₆), also show little consistency between the samples tested. In all cases, however, these gases are present for only a small fraction of the total microwave reaction time.

The total amounts of each gas released are listed in Table 1. Analysis has shown that the gases, carbon monoxide, methane, carbon dioxide, and ethylene are present in all cases. Small amounts of acetylene and ethane were identified in some of the samples. With the exception of samples A10 and A7 the volume of carbon dioxide exceeds that of all other gases produced. This is probably a result of combustion of the hydrocarbons released during the heating process. This is evident by the observation of a bright blue flame during the heating of the samples.

Samples injected into the chromatograph after reaction times of 30 seconds to 1 minute did not reveal any gaseous products. This would seem to indicate that there was a time delay at the start of each heating test before any significant amount of gas was released from the sample being heated.

During the testing procedure, the first sign of gases being released was a yellowish-grey smoke after only 15–20 seconds of reaction time. This can account for part of the delay. The remaining portion can be attributed to the travelling time from the reactor vessel to the sample loop.

Table 2 shows a comparison between the results of the microwave tests and those determined by Fischer assay. The total weight losses for all samples tested by the microwave procedure were higher than those for the same samples tested by Fischer assay. This is due solely to the significantly greater quantity of gas produced by the microwave reactor method. The gas yield ranged from a low of 1.1 times to a high of 11.3 times that of the Fischer assay. The reason for such high gas yields was that reaction temperature is approximately twice that used in the standardized technique. By reducing the temperature, it would be possible to reduce the gas yield and increase the oil yield. The oil yield by the microwave process averaged 90.6% of the Fischer assay yield. By comparison, the process used to recover oil from the tar sands of Alberta has a recovery rate of approximately 73%.

Results of the tests to determine the percentage of extracted bitumen as a function of reaction time are shown in Fig. 3. All samples show a very consistent behaviour. Weight loss was very rapid during the initial stages of the reaction period. The length of time this initial stage lasted was generally related to the oil content of the samples being heated. The higher the Fischer assay oil yield, the longer was this initial period. After the end of this stage, the percentage extracted changes very little over the remaining reaction time.

The total weight losses after a minimum reaction time of 16 minutes ranged from a low of 6.5% for the lean sample, A2, to a high of 38.4% for the rich sample, A1. As anticipated, the richer the sample, the higher the percentage of bitumen extracted. The form of behaviour exhibited by all samples was in agreement with similar observations made on microwave-heated Athabasca tar sands [1].

NET ENERGY RECOVERY

Bridges et al. [2] have argued that in-situ microwave heating is impractical due to inefficient spatial distribution in the application of energy. They have looked at RF application in situ and calculated a net energy recovery (NER) for the process. We shall consider using microwave heating in an above-ground retort with specifically designed applicators and calculate the NER for this process based on their method. A moderate grade shale, sample A3 (22.2 U.S. gal/ton) is chosen for illustration.

In performing the calculation the following assumptions will be made:

- (a) The 60-Hz power used in the process is generated on site by combustion of liquid or gaseous products from the process with an assumed efficiency of 40%.
- (b) The 60-Hz energy is converted to microwave energy with an efficiency of 85% although this could improve with advancing technology.
- (c) A 90% efficiency is obtained in transmission of microwave energy into the shale (95% has been predicted by Bridges et al. [2]). Conveyor-fed applicators could be designed to achieve this.
- (d) Shale at 22.2 U.S. gal/ton requires 0.650 MJ/kg (280 BTU/lb) to reach pyrolysis at 500°C with 25°C initial temperature [2].
- (e) Some fraction, k , of heat in the spent shale is recycled to improve overall process efficiency, based upon a heat content of 0.487 MJ/kg (210 BTU/lb) at 500°C [2].
- (f) An 89.3% recovery of the Fischer assay in the liquid oil form is used and all oil produced is recovered.
- (g) Gaseous by-products produce 1.814 MJ/kg of shale from sample A3 as detailed in Table 3.
- (h) Energy used in mining and transport of material is not considered. Also not considered is energy available in additional gaseous by-products produced if steam or H₂ gas is injected into the retort during processing to gasify the residual carbon in the spent shale.

Figure 4 shows an energy flow diagram which assumes an input of 1 kg of sample A3 and recycling of a fraction, k , of heat in the spent shale. All quantities are expressed in megajoules. With the exception of specific heat data taken from Bridges et al. [2], all data and constants are taken from Tables 1 and 2.

If the fraction, k , of waste heat recycled were changed it would affect the NER. This can be made a general expression in terms of the fraction k .

$$\text{Net energy output} = 3.058 \text{ liquid} + 1.814 \text{ gas} = 4.872 \text{ MJ.}$$

Net energy input = $2.124 - 1.337k$ MJ.

Net energy ratio (net energy out/net energy in) is given by

$$\text{NER} = \frac{4.872}{2.124 - 1.337k}$$

The NER varies from 2.3 with no waste heat recovery to 3.7 for 60% recovery, while a more realistic 40% recovery would produce a NER of 3. For sample A10 (61.5 U.S. gal/ton) the NER could approach 10. Unlike the in-situ process from which this model is taken all the oil produced is recovered. Recycled heat could be more efficiently employed than in an in-situ process, for instance, to dry and preheat incoming shale. Any gasification of residual carbon would only further improve the efficiency of the process.

CONCLUSIONS

Microwave heating of small New Brunswick oil shale samples has shown that 90% of the Fischer assay oil content can be extracted, while up to eleven times the gaseous by-products can be produced. Processing at a slower rate would increase the oil content, while decreasing the amount of gas produced. The gases carbon monoxide, carbon dioxide, methane, and ethylene were found in all samples, while ethane and acetylene were found in some samples.

A net energy recovery ratio of 3 is predicted if 40% of the waste heat could be recovered from a moderate grade shale. Higher grade shale would produce better results, possibly as high as 10 NER.

In this work no attempt was made to optimize the efficiency of the process, nor to investigate a continuous flow process. Further work on these aspects is required before economic feasibility can be determined.

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