

## EXTRACTION OF HYDROCARBONS FROM ANTRIM OIL SHALE

J. P. Humphrey  
Oil Shale Research Project  
734 Building  
Dow Chemical U.S.A.  
Midland, MI 48640

### ABSTRACT

The Dow Chemical Company has performed a variety of in situ experiments on the Antrim oil shale which underlies Michigan. These experiments have ranged from in situ combustion in a quarry to attempted extraction at a depth of 2,600 feet (780 m).

Currently, Dow is continuing its efforts to obtain hydrocarbons from this resource on a four-year contract (Contract No. EX-76-C-01-2346) in cooperation with the Department of Energy. A site, prepared through explosive fracturing, is being tested. Extensive permeability tests have been performed and attempts have been made at initiating partial combustion within the formation.

Extensive laboratory experiments have been coupled with Dow's efforts to recover hydrocarbons in situ. These tests have been carried out under a variety of different atmospheres, pressures, and temperatures and in various types of apparatus. In general, results show that hydrocarbons can be extracted in many ways and the products produced and yields obtained will vary accordingly.

### INTRODUCTION

As early as 1955, research planners for The Dow Chemical Company expressed concern over long-term availability of naturally occurring hydrocarbons for fuels and feed stock in certain parts of the country. Many alternative sources were examined; among these was the recovery of oil and gas from oil shale. A block of oil shale was eventually purchased in Colorado for future

exploitation, and an extensive research program was also initiated to examine the potential of the vast (Devonian) oil shale deposits of the eastern and mid-western United States.

No Dow development of the Colorado shale tract ever occurred and it has since been sold. Research efforts on Devonian shales resulted in four major field experiments and many, many different laboratory measurements. While these laboratory and field results may not be truly indicative of what might occur while attempting extraction on a large, commercial, above-ground or below-ground (in situ) process, they do give some insight into the physical and chemical behavior of these oil shales. The reader is left to compare these results, for the most part, with similar measurements made on western (Green River) oil shales that have been so extensively reported in the literature.

### GEOLOGY

Devonian shales of the east and mid-west cover an extremely vast area (fig. 1). These shales are known by various names in different parts of the country. Chattanooga, New Albany, Woodford, Ohio and Antrim (in Michigan) are just a few of the better known ones. Dow Chemical performed preliminary, resource assessments on these shales in several states but eventually attention was focused on the Michigan Antrim. The Antrim offered the advantage of being

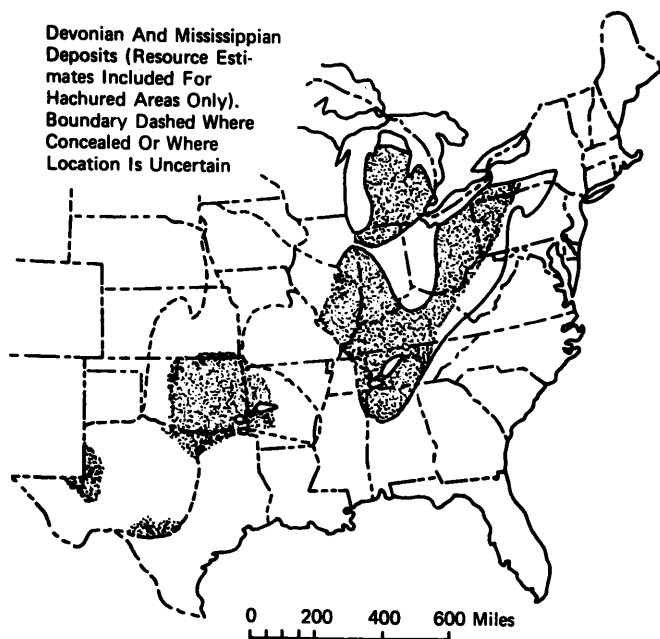


Figure 1. Devonian and Mississippian oil shale deposits in the east-central United States.

located around Dow's founding location in Michigan and is approximately one-half mile (0.8 km) below our Midland plant site.

The Antrim is a black, bituminous shale

deposited some 260 million years ago in a shallow marine sea which covered much of the east central part of the continent during late Devonian and early Mississippian time. In Michigan, the black shale interval includes the black Sunbury and the Antrim, with an intervening sand and gray shale wedge of Berea-Bedford in the eastern part of the lower peninsula (fig. 2). In the western part, there is a facies change from black shale to the gray-green shales of the Ellsworth which interfinger with the black shales in the central part of the State. The Ellsworth thickens to the west.

The Michigan Basin, in which the Antrim was deposited, was a large negative area, sinking throughout early Paleozoic time. The Antrim outcrops at the surface in Antrim, Charlevoix, and Alpena Counties, Michigan, and in Lambton County, Ontario. At Midland, it is 2600 feet (780 m) below the surface, dipping yet deeper to the center of the basin, northwest of Midland.

Mineralogical studies have shown the Antrim to be a very fine-grained, lami-

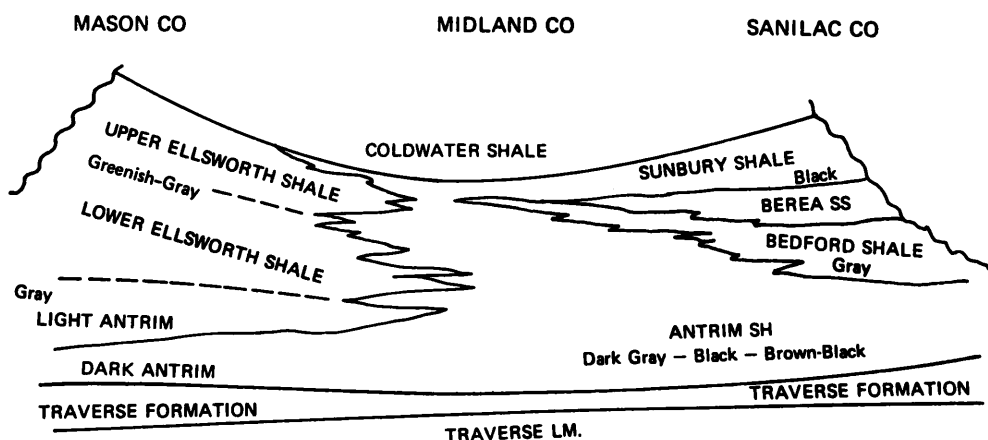


Figure 2. West to east schematic cross section showing general facies relationships.

nated shale, composed dominantly of the clay-mineral illite and quartz with minor amounts of organic matter, pyrite and carbonate. The clay-mineral mica or illite occurs as thin platelets, 1 to 12 microns in thickness, and about 5 to 35 microns in major diameter. Quartz and feldspar, mainly microcline and sodic plagioclase, occur as grains, 5 to 30 microns in size. The organic matter occurs as a finely dispersed, amorphous brown binder and as the disc-shaped, spore-like fossil, Tasmanites. Pyrite ranges from large concretionary masses to very finely disseminated crystals, the bulk of which range in size from less than 0.5 microns to 15 microns. Dolomite and calcite are in roughly equal proportions and occur as minute, irregular grains. Traces of chlorite, tourmaline and zircon have been identified.

Elemental analyses of composite samples made up from well cores are shown in table 1: carbon, sulfur and hydrogen analyses are shown in table 2.

Table 1. Analysis of composite from raw Antrim shale cores.

	<u>Wet Chemical Analysis</u>	
% Ignition Loss 900°C	12.05	12.13
% SiO <sub>2</sub>	57.14	57.23
% Al <sub>2</sub> O <sub>3</sub>	12.29	12.46
% TiO <sub>2</sub>	0.40	0.40
% Fe <sub>2</sub> O <sub>3</sub>	5.45	5.35
% CaO	3.13	3.11
% MgO	1.70	1.64
% MnO	0.04	0.04
% K <sub>2</sub> O	4.37	4.32
% Na <sub>2</sub> O	0.32	0.33
% Total S	2.07	2.02
% U	0.0019	0.0022
% Th	0.010	0.011
	<u>Emission Spectroscopy</u>	
% Cu	0.03	0.06
% Ni	0.01	0.02
% V	0.06	0.08
% Rb	0.02	0.03

Table 2. Analyses of "standard blend" of chemical well Antrim shale.

<u>Laboratory</u>	<u>Special Services(574)</u>	<u>East Main(294)</u>	<u>West Main(143)</u>
% C (total)	6.42	6.40	6.55
% C (carbonate)	0.67	0.70	0.70
% C (combustible)	5.75	5.70	5.85
% H	1.03	0.92	0.98
% S (total)	1.93	2.14	2.06
% S (sulfide)	0.002	0.02	0.009

#### NATURAL GAS OCCURRENCE

Of all the potential values in the black shales of the central United States, natural gas has been the most important. Natural gas is produced in commercial quantities from fractured reservoirs in Ohio and Kentucky and has been logged in the Antrim section throughout Michigan. A small Antrim gas field is in operation in Otsego County and produced 117,470,000 cubic feet (39.1 million m<sup>3</sup>) in 1973.

Dow's early work was directed at natural gas production from the Antrim. One well, drilled and sand fractured in Otsego County, Michigan, gauged between seven and ten million cubic feet (266,700 m<sup>3</sup>) per day. An impressive volume for a shale gas well. Later treatments reduced this to less than four million. Other wells were drilled in other areas, but none produced commercial quantities of natural gas.

In any case, these shales do contain significant quantities of gas trapped in the pore structure and gas will evolve from fresh core material naturally. The analysis, shown in table 3, is of gas being evolved from a core at two different times and gas found evolving from the same well at the wellhead. Some of the unsaturates reported may only be a result of the analytical procedure. Also, there

Table 3. Core and wellhead gas analysis, (percent by weight).

COMPONENT	CORE GAS*		WELLHEAD GAS
	Time 1	Time 2	
Carbon Dioxide	-	-	0.1
Helium	0.02	0.03	-
Hydrogen	0.54	0.56	-
Nitrogen	8.82	5.51	8.74
Methane	70.27	75.50	70.65
Ethylene	1.53	-	-
Ethane	9.79	12.20	13.13
Propane	5.68	4.75	5.29
Butene	0.26	0.04	-
Butane	1.81	0.95	1.69
Pentene	0.28	0.08	-
Pentane	0.67	0.23	0.45
Hexene	0.13	0.02	-
Hexane	0.17	0.05	0.05
Mass 68	0.03	-	-
Mass 82	-	0.02	-

\*Four volumes of gas evolved per volume of shale

is some possibility of air contamination, so the results should be taken only as an example. During these de-gassing experiments, it was found that about four volumes of gas are given up per volume of shale. With sufficient fracturing, either natural or induced, gas can be recovered.

The porosity of raw Antrim shale is on the order of five percent with 70 to 90 percent of the pores being smaller than 100 Angstroms. To open up this pore volume, or create sufficient surface area for natural flow of gas, will require massive fracturing. On the other hand, retorting under a variety of atmospheres increases porosity to about 20 percent and increases permeability significantly, depending upon the amount of thermal fracturing. At least this occurs in the laboratory.

#### SHALE RETORTING UNDER HYDROGEN

Direct hydrogenation of Antrim shale was performed to determine if aromatic hydrocarbons could be formed from shale under the

proper conditions. Results showed that raw Antrim shale, retorted under hydrogen pressure [starting H<sub>2</sub> pressure about 700 psig (4.9 MPa), operating pressure about 1500 psig (10.5 MPa)] in a pressurized bomb for about 5 hours, at a temperature of about 450°C, yielded primarily aromatic and condensed aromatic (both alkylated and unalkylated) hydrocarbons; whereas, retorting at lower temperatures produced largely aliphatic products. Lower total hydrocarbon yields and a lower degree of gasification also occurred at the lower temperatures. Later, it was shown that shale oil could be aromatized in the presence of spent (hydrogen-retorted) Antrim shale. Still later, it was found that paraffin wax, crude petroleum, bright stock, and even polyethylene could be aromatized and that the presence of shale was not required. It was concluded that aromatization of nonaromatic stocks was caused by their prolonged exposure to high temperature.

Several experiments were run, using different atmospheres, to test the hypothesis that the atmosphere is one prime variable. These results are shown in table 4.

Hydrocarbon and sulfur (H<sub>2</sub>S) yields from hydrogen retorting were, respectively, 5.50 and 1.83 percent. Retortings under argon pressure or with no added gas gave hydrocarbon yields less than half as great as those obtained from hydrogen retortings. Retortings under steam pressure were only slightly, if at all, better. These observations were made for both shale and marlstone.

Yields from a shale, retorting under CO pressure, approached those from a hydrogen retorting because H<sub>2</sub> was formed by the reaction of the CO with water in the shale. High yields of sulfur, as H<sub>2</sub>S, accompanied the high hydrocarbon yields. The marlstone, although yielding at best more than twice as much hydrocarbon as the shale, gave less than one-sixth as

Table 4. Comparison of various atmospheres.

<u>Antrim Shale:</u>	<u>Atmosphere</u>	<u>Yields (% of Charge)</u>			
		<u>Hydrocarbon Liquor</u>	<u>Hydrocarbon Gas</u>	<u>Liquor + Gas</u>	<u>S</u>
	H <sub>2</sub>	2.83	2.67	5.50	1.83
	Ar	0.89	1.78	2.67	
	Ar	0.43	1.26	1.69	0.69
	-	0.81	1.16	1.96	1.23
	H <sub>2</sub> O	0.95	2.27	3.22	
	H <sub>2</sub> O	0.925	2.01	2.94	1.13
	CH <sub>4</sub>	0.92	-	-	0.83
	CO	1.60	2.57	4.17	1.15
<u>Colorado Marlstone:</u>	H <sub>2</sub>	6.80	5.85	12.65	0.28
	Ar	2.69	3.29	5.95	0.06
	-	2.5	3.41	5.9	0.14
	H <sub>2</sub> O	2.29	3.43	5.72	0.06

much sulfur. Carbon and sulfur contents of the raw and spent shales are shown in table 5.

Table 5. Comparison of hydrogen vs. inert gas retorting.

	<u>Combustible Carbon</u>	<u>Total Sulfur</u>	<u>Sulfide Sulfur</u>
Raw Shale	8.70%	4.45%	0.00%
H <sub>2</sub> - Retorted Shale	3.03%	2.74%	1.96%
Shale Retorted Without Gas	6.57%	4.90%	1.63%

Shale analyses showed only 35 percent of the shale's original combustible carbon remaining in the hydrogen-retorted shale, whereas, 75 percent of the original combustible carbon remained in the shale after the "gasless" retorting. Hydrogen retorting also removed 38 percent of the shale's sulfur content as volatile products. Yields from hydrogen retortings of Alpena Antrim

shale, at various temperatures, are shown in table 6.

Although many time-temperature conditions were not investigated, several conclusions were, nevertheless, readily apparent from the results. Retorting was very incomplete even after 6 hours at 375°C, but temperatures of 400°C and above showed much higher rates. The weight ratio of gaseous to liquid hydrocarbons rose sharply and continuously from 0.25 at 400°C to 6.8 at 570°C. Highest hydrocarbon yields were obtained at 450° and 475°C; the yield from a 2-hour run at 475°C being 6.19 percent. A reduction, not attributable to a reduction in reaction time, occurred at 500°C. In all runs in this set and the preceding one, the reactor was heated rapidly to the desired temperature by immersion in a hot lead bath. Rapid heating, at higher temperatures, may have caused excessive losses in the form of nonvolatile hydrocarbons or coke.

Table 6. Yields from hydrogen retorting.

Temperature	Time	Yields (% of Charge)			
		Hydrocarbon Liquor	Hydrocarbon Gas	Liquor + Gas	S
375°C	6 Hours	1.67	0.50	2.17	1.27
400	4 Hours	3.52	0.87	4.39	1.41
450	4 Hours	2.83	2.67	5.50	1.83
475	2 Hours	2.49	3.70	6.19	1.13
500	2 Hours	1.30	3.15	4.45	0.96
525	1.5 Hours	1.11	3.14	4.25	1.07
550	1 Hour	0.65	3.03	3.68	
570	45 Minutes	0.47	3.19	3.66	1.04

Gas-chromatographic examination of the liquid products from these and other runs showed that aromaticity increased with lower H<sub>2</sub> pressure, greater contact time, higher temperature, or lower ratio of charge to reactor volume. In the liquid products from runs made above 500°C, no aliphatics were seen. Above 550°C compounds, such as benzene, naphthalene and phenanthrene predominated, with little alkyl substitution. In the gaseous products, methane increased, at the expense of higher hydrocarbons, as retorting temperature was increased.

A shale sample was retorted at 350°C in an atmosphere corresponding (on a basis of the materials initially added) to 40 percent H<sub>2</sub>, 25 percent CO<sub>2</sub>, and 35 percent H<sub>2</sub>O. A two-hour exposure, at a total pressure of 1500-2000 psig (10.5-/4 MPa), was used. After this retorting, the same shale sample was retorted in a fresh atmosphere of the same composition. The process was repeated at progressively higher temperatures until additional retorting failed to produce additional oil. The aim of this study was to simulate the effects of a gradual heating of a region in the Antrim formation which would be brought about by the advance of a "front" of hot gases having the stated composition.

Five separate samples of shale were treated in this manner, and the following conclusions were reached:

- (1) Approximately 5 percent of the weight of this shale can be recovered as oil and hydrocarbon gas under these conditions.
- (2) Retorting at 350°C liberates more than half as much H<sub>2</sub>S, but less than one-fourth as much oil, as can be liberated by retorting at 450° or 475°C.
- (3) A shale which has been exhausted of oil-forming materials by hydrogen retorting may still yield hydrocarbon gases when hydrogen-retorted at a still higher temperature.

In these runs, a significant, although minor, fraction of the total oil yield was produced at 350°C by the first retorting; much less appeared at the 375°C retorting, although yield rose again at 400°C.

A series of pairs of steam retorting were also made on samples of this shale. In each pair of retortings, a charge was first retorted at 375°C for 4 hours, then retorted again for 2 hours at 450°C, both retortings taking place in the presence of added water. Average hydrocarbon and sulfur yields were, respectively, 2.07 and 0.67 percent of the shale's weight.

Highest hydrocarbon yield from a sample of this shale was 4.2 percent, and was obtained by a pair of hydrogen retortings; one at 350°C, followed by one at 500°C. Retorting pairs at 450° and 500°C; at 360° and 475°C; and at 335° and 525°C, all gave hydrocarbon yields in the vicinity of 4 percent.

Low-temperature oxidation studies were also made on raw shale in an attempt to determine minimum temperatures at which self-sustaining oxidation would begin. At an initial O<sub>2</sub> pressure of 1500 psig (10.5 MPa), a self-sustaining oxidation began at 107°C. When initial O<sub>2</sub> pressure was 500 psig (3.5 MPa), oxidation began at 125 or 130°C. An aqueous product from this run contained several percent each of acetic acid and methanol.

Shale oil, obtained from air retorting during one field experiment, was also hydrogenated in the presence of various commercial Co-Mo catalysts, much as petroleum fractions are. Recovery of oil exceeded 80 percent by weight. Hydrogenated oil was lighter in color, more transparent, less viscous, and less dense than crude oil. Hydrogenation was shown to reduce the crude shale oil's 4.79 percent sulfur content by one to two orders of magnitude, and its 0.68 percent nitrogen content by a factor of 2 to 5. The oil's crackability (ethylene yield and relative freedom from coke formation) was markedly improved.

#### RETORTING UNDER AIR, NITROGEN, STEAM AND CARBON DIOXIDE

Previously described retorting results were produced in closed bomb experiments. In addition, retorting has been carried out under flowing conditions, using small cubes of shale, in the apparatus shown in figure 3. These experiments were limited to atmospheric pressure, but were very enlightening as to the evolution of products with time, under a variety of atmospheres. The results produced are very detailed and will be reported in a later paper. Only the general conclusions will be given here.

Product gas heating values are used for comparison; absolute values, however, have no meaning since the diluent flow was essentially arbitrary.

Cubes, pyrolyzed under nitrogen, showed peak heating value (including nitrogen) was increased from 120 Btu/scf at 500°C to 600 Btu/scf (21kj/m<sup>3</sup>) at 700-750°C. This reflects both reduced gas yields and lower heating rates at lower temperatures. Peak hydrocarbon evolution (figure 4) occurred after 13-15 minutes at 500°C. This was reduced to 7 minutes (420 sec) at 600°C and 4 minutes (240 sec) at 700°C. Block heating times are an important lag at high temperatures. Pyrolysis was generally complete after 10 to 20 minutes (600-1200 sec). Products were obtained primarily as condensables (oils) at low temperatures, and as volatiles (gases) at high temperatures. About 45 to 65 percent of the carbon remained in the block after pyrolysis under nitrogen.

The ability of Antrim oil shale to leave large carbon residues was previously shown when retorting under various inert atmospheres. It is also interesting to note that large carbon residues are also left behind during Fischer Assay as it is an inert retorting of the shale. Figure 5 shows the assay of a core taken from Dow's Midland, Michigan, plant. Residual carbon left after retorting, correlates fairly well with oil content. These large residues are the reason that Fischer Assay is not a good method for measuring hydrocarbon yield; much of this carbon can be used during retorting under both oxidizing and reducing conditions.

Also shown in figure 5 is the poor point of oil recovered from the assay. The low pour points are fairly typical of oils recovered from these Devonian shales. Similar oils have also been examined from other retorting procedures and, in general, show a low pour

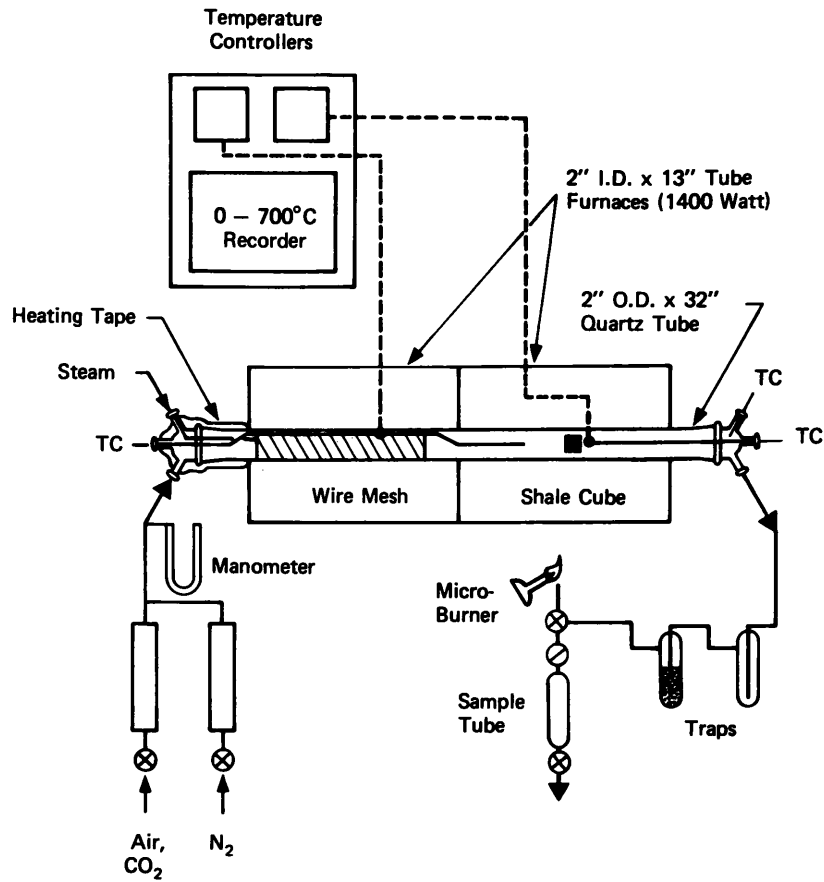


Figure 3. Schematic of block retort.

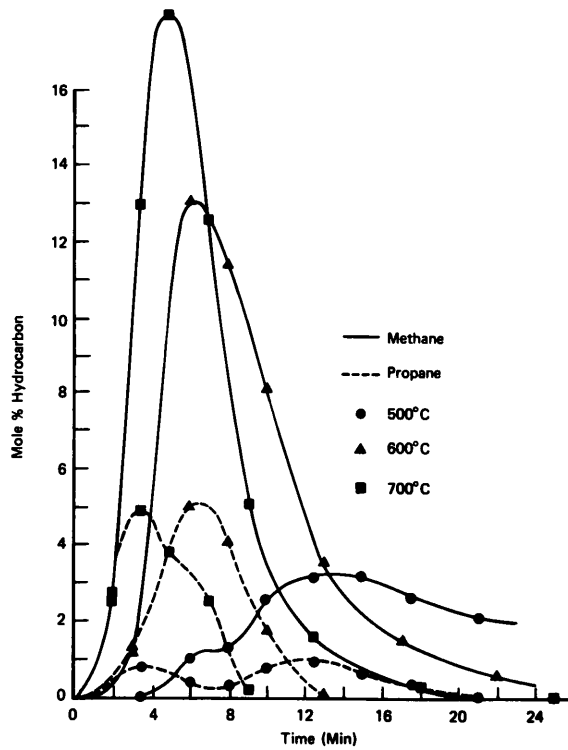


Figure 4. Methane and propane evolution at various temperatures, 500 sccm N<sub>2</sub>.



CORE ANALYSIS

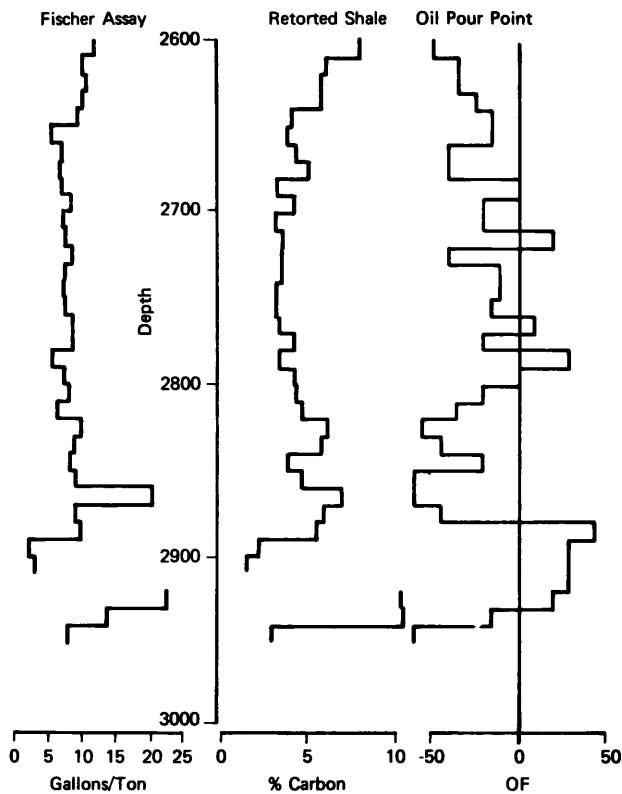


Figure 5. Nitrogen and sulfur distributions in raw Utah shale oils.

point. This makes the oil very easy to handle during further refining.

In experiments using air, oxygen levels were low during peak hydrocarbon evolution. At low temperatures (500 - 550°C), hydrocarbon evolution and heating value were increased compared to runs under nitrogen (figure 6). At high temperatures (700 -

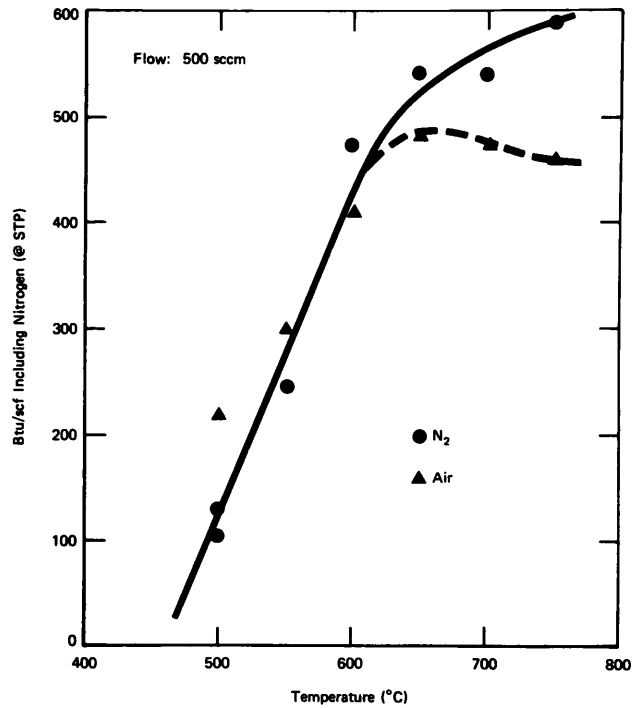


Figure 6. Comparison of peak offgas heating values under air and nitrogen.

750°C), the heating value dropped from 600 to 450 Btu/scf (21kj/m<sup>3</sup>-15.8kj/m<sup>3</sup>) compared to runs under nitrogen. Only about one-fourth to one-third of the residual carbon in the block was burned out in one hour. Later experiments showed that up to 10 hours would be required to exhaust 90 percent of the carbon at 600°C. Mass transfer of oxygen into the shale is rate limiting during combustion. Finally, in experiments using carbon dioxide and steam (figure

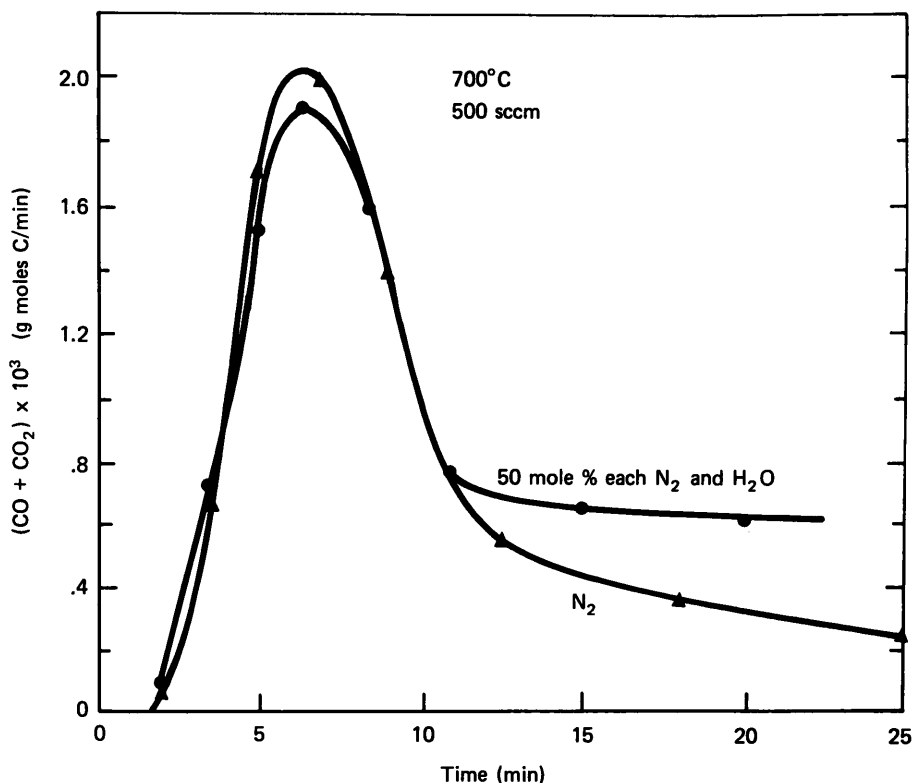


Figure 7. Comparison of carbon oxidation under nitrogen and nitrogen/steam.

7), some utilization of carbon residuals was observed, but rates were slow compared to oxidation; possibly limited either kinetically, thermodynamically or by diffusion.

#### SUMMARY

The black Devonian shales of the central United States are a vast resource from which hydrocarbons can be extracted by retorting with air, oxygen, steam, hydrogen carbon monoxide or under inert gas atmospheres. The poorest carbon utilization occurs under true pyrolysis conditions because these shales, as evidenced from results on the Michigan Antrim, tend to coke, leaving behind much of the available carbon.

By varying retorting conditions, time, temperature and atmosphere, the products produced can be varied from aliphatic to aromatic and from dominantly gases to oils. Oils, produced under most conditions, are very light and show a very low pour point for a shale-derived oil.

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