

Final Report

OILS AND TARS FROM IOWA SHALES

by

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EXPERIMENT
STATION

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INTRODUCTION

The inadequate supply of suitable road surfacing material in the southern part of Iowa raises the question of the possibility of utilizing certain shales abundant in this area. These carbonaceous shales commonly overlie the coal beds and may also be found as impurities in the coal seams. They constitute the "slate" which with minor amounts of coal makes up the "gob" piles at the mines. These shales frequently contain enough carbonaceous material to burn. Those which do not usually require only a relatively small amount of coal mixed with them to support combustion. As a result, the "gob" piles frequently burn. The residual shale material is frequently used locally as a road surfacing material. However, since there is no control over the burning, there is no assurance that the product is the most suitable which might be produced or that it is even uniform in its properties.

To determine if a controlled burning would produce a suitable road building product economically a research project "Use of Shales as Highway Materials" (ISHC Project HR-21, IEES Project 299-S) was set up in the Iowa Engineering Experiment Station with funds provided by the Iowa State Highway Commission. This project was supervised by Charles Frush, formerly Assistant Professor of Mining Engineering at Iowa State University. The various shales were subjected to controlled burning, and the solid residues were tested for their suitability for highway use.

Since the partial combustion of a carbonaceous material such as that found in the shales usually produces oils and tars as by-products, it

seemed desirable to investigate the identity of the by-products produced from the shale burning. It appeared possible that these might have sufficient value to make recovery profitable. As a result, another project in research, "Oils and Tars in Iowa Shales" (ISHC Project HR 32, IEES Project 318-S) was set up. The results of the work under this project are the subject of this report.

The research work was divided as follows:

- I. Extraction of the shale by solvents
- II. Recovery of products from partial combustion of the shale
- III. Recovery of products from destructive distillation of the shale

THE RAW MATERIAL

The choice of raw material for this study is discussed by Frush (5) as follows:

"That part of Iowa in which natural aggregates, and particularly limestone, are not abundant corresponds generally to that part of the state which is covered by Pennsylvanian sediments. These consist predominantly of clays and shales, with smaller quantities of sandstone, limestone, coal, and related materials. Many of the shales are bituminous, particularly those associated with deposits of coal, the bituminous content being quite variable, ranging from almost none up to major amounts. These shales were chosen for study because of their wide distribution, abundance, the inherent fuel content, and their lack of value for other uses."

The shales used in these studies were obtained by Professor Frush and the author from various southern Iowa coal mines (figure 1) The original group of samples, numbered II-B-1 to II-B-18 inclusive, are listed in table I with their calorific values and some chemical characteristics. Samples II-B-20 to II-B-23 were collected by the author in March, 1958. They are similar.

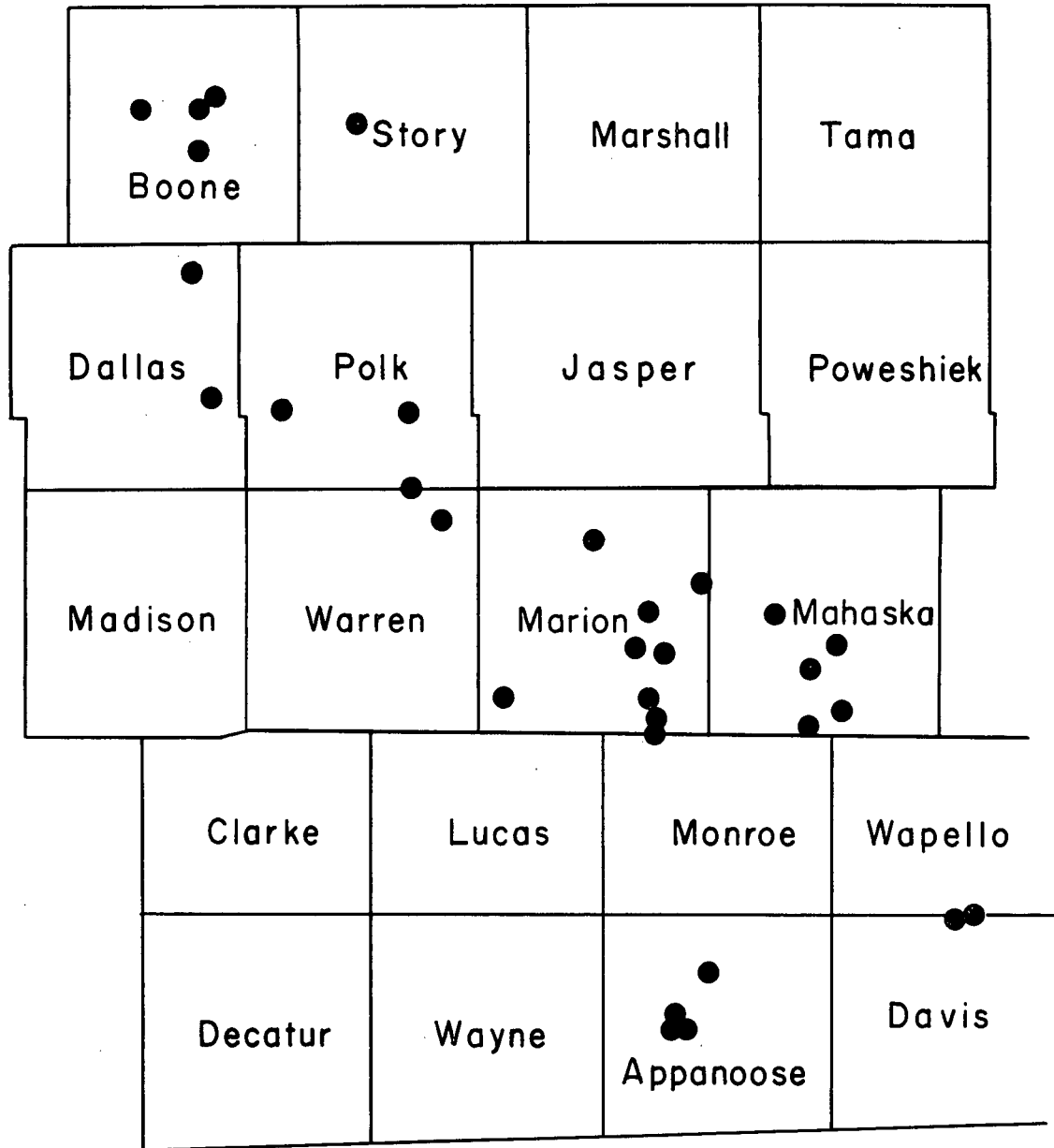


Fig. 1. Sources of samples.

to IIB10, a new sample of which was also collected. Numbers IIB24 to IIB26 were applied to samples previously identified by location name.

SOLVENT EXTRACTION STUDIES

The possibility of extracting useful organic material from the shale prior to heat processing was studied in a preliminary manner. Three samples were investigated: No. II-B-9, with a calorific value of 520 Btu.; No. II-B-10, with a calorific value of 6050 Btu.; and No. II-B-15, similar to II-B-10. The five solvents were: hexane petroleum fraction, benzol, trichloroethylene, perchloroethylene, and methylene chloride.

The samples were first ground to a suitable size (table II) and then extracted in Soxhlet apparatus for periods of two and four hours with results shown in table III. A 1000 gram sample of No. II-B-10 was extracted successively with three 1500 ml batches of trichloroethylene. Each extraction was continued for two hours. Distillation and redistillation of the total extract resulted in a product boiling at 96°C or over, representing about 0.8 percent of the shale and a fraction boiling at 86.5° to 96°C , representing another 0.5 percent of the shale. The remainder of the extract was apparently solvent. The total of 1.3 percent checks well with the 1.23 percent secured by Soxhlet extraction.

The amounts of extract secured by both types of extraction are too low to show promise of the shale as a source of extractable material. It is possible that other solvents might produce more promising results. However the solvents included representative examples of a common aromatic solvent (benzol), an aliphatic hydrocarbon (hexane), unsaturated chlorinated hydrocarbons (trichloroethylene and perchloroethylene) and a saturated chlorinated hydrocarbon (methylene chloride).

RECOVERY OF PRODUCTS FROM PARTIAL COMBUSTION OF THE SHALE

In the parent project "The Conversion of Iowa Shales into Road-Making Materials" under Professor Charles Frush, shale was heated under different conditions to produce a road-making material. A considerable part of this work involved the burning of all or part of the combustible material in the shale itself to provide heat for the process. Some of the burning operation was carried out in piles of shale out-of-doors. Other batches of shale were burned in the laboratory under controlled conditions.

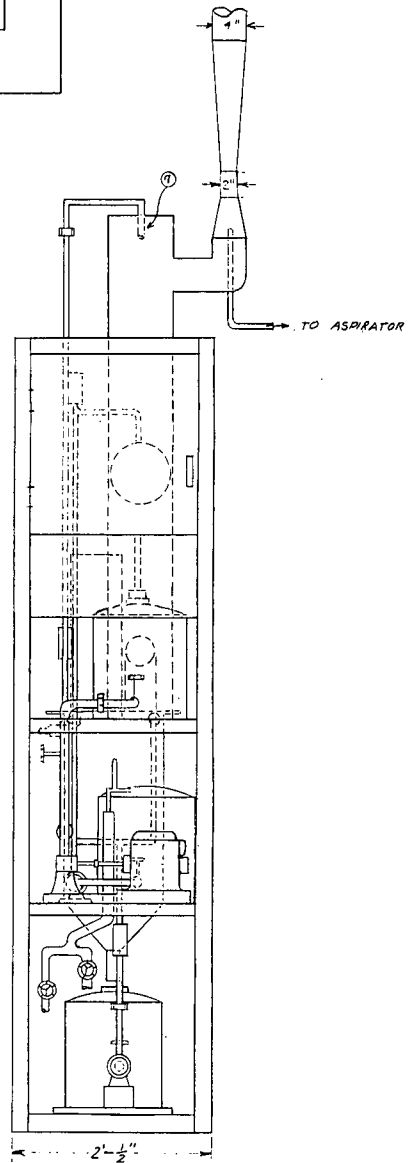
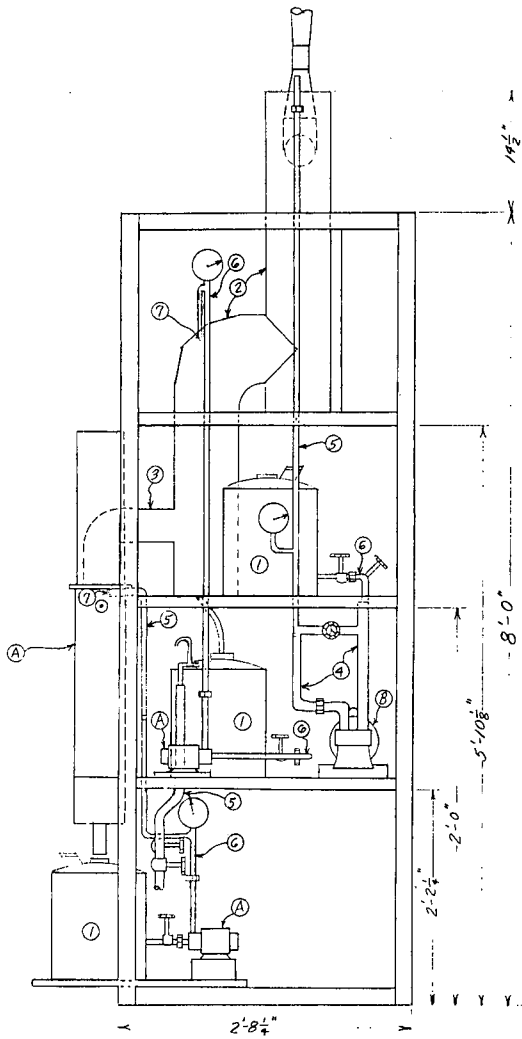
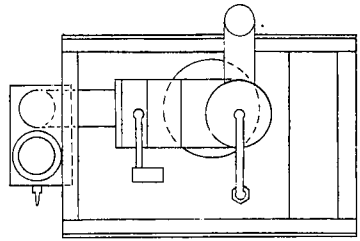
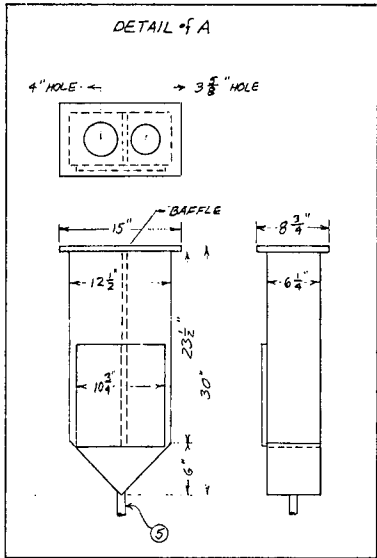
Part of the experiments were carried out in an automatically controlled retort with a capacity of approximately eight pounds of shale. Other experiments utilized a pilot plant sized retort which was basically a vertical steel cylinder two feet in internal diameter and ten feet tall (4) (5). Frush noted the gaseous products of combustion and commented upon them. He constructed equipment designed to recover the combustion products. This equipment (4) was turned over to the new project.

EQUIPMENT

The small retort was connected to the absorption equipment shown in figures 2 and 3. The gases of combustion from the retort under suction of the aspirator passed down into the spray chamber shown in "Detail of A." Here they passed through a hot water spray under the center baffle leaving at the top on the opposite side. The purpose of this spray chamber was to condense and entrap high boiling products.

From the hot spray chamber the gases passed into the second chamber in which a cold water spray condensed products with lower boiling points. The third chamber was packed with Berl saddles over which "Oleum Spirits" (a petroleum fraction somewhat heavier than kerosene) was sprayed. This was

I.E.S.S.
 PROJECT 818-S
 OILS AND TARS FROM IOWA SHALE
 STACK GAS ADSORPTION TOWERS
 SCALE: 1" = 1'-0"
 DRAW. NO. 100-111
 OCTOBER 19, 1954



- KEY
- 1 - 5-GALLON CANS
 - 2 - 8" SHEET METAL PIPE
 - 3 - 4" " " "
 - 4 - 1/2" STEEL PIPE
 - 5 - 3/8" STEEL PIPE
 - 6 - 1/4" STEEL PIPE
 - 7 - SPRAYS

A-EASTERN INDUSTRIES PUMP, MODEL Q-1
 B-VIKING PUMP MODEL Z.F.H. 0365307 1/2 in.

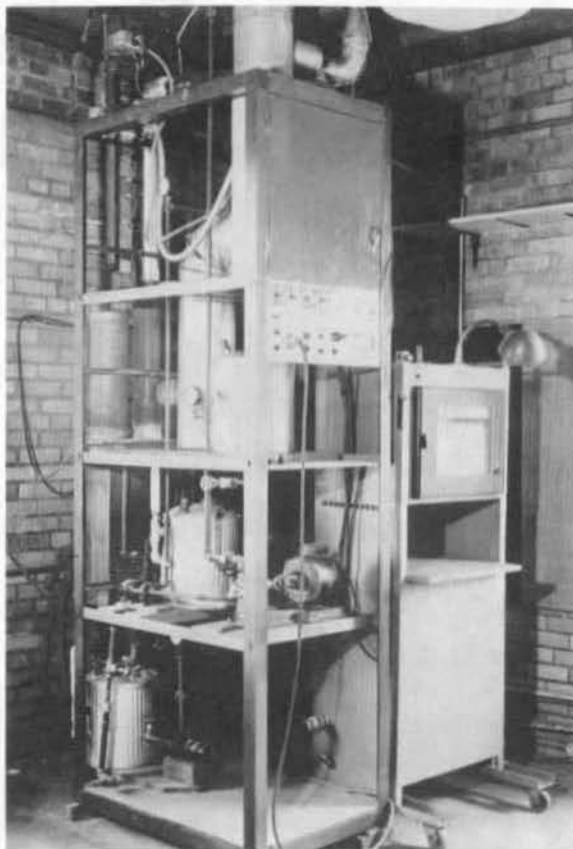


Fig. 3. Partial combustion equipment.

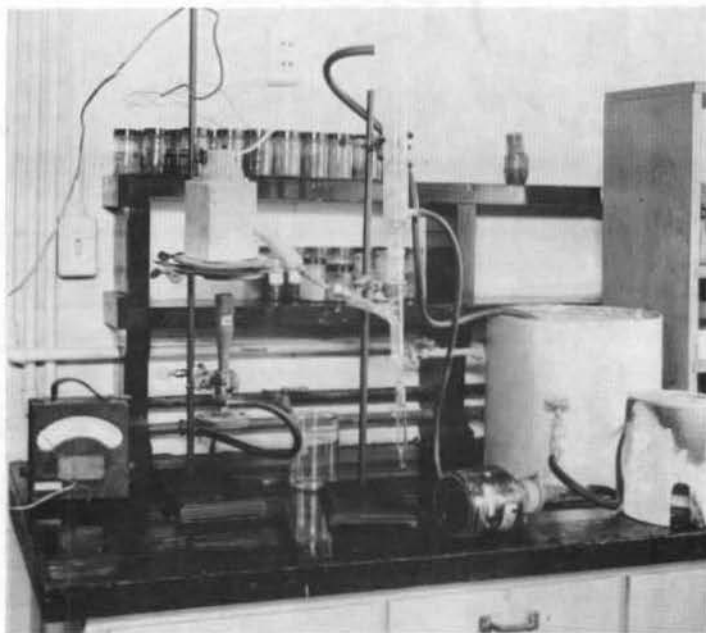


Fig. 4. Fischer retort assembly.

designed to absorb very volatile organic vapor and to dissolve other organic compounds not thrown out in the water sprays. The spray liquid from each of the chambers was circulated back continuously from the receiving cans by pumps. After preliminary runs the "Oleum Spirits" in the third spray chamber was replaced with perchloroethylene. Since the perchloroethylene had a definite constant boiling point it was assumed that any dissolved material could be separated from it more readily by distillation than from the "Oleum Spirits" which was a mixture of hydrocarbons.

EXPERIMENTAL PROCEDURE

The shale was ground and sized to pass a 3 mesh opening and be retained on an 8 mesh opening. A charge of approximately 6 pounds was placed in the retort. The aspirator was turned on to draw air through the retort and the 3 spray chambers. The sprays and the recording potentiometer were turned on. The shale was ignited with a Meeker burner. The shale was allowed to burn with the run ending when the temperature dropped in the retort as shown on the temperature recorder (potentiometer).

The liquid from the spray chambers on part of the runs was fractionally distilled in the chemical laboratory to separate any recovered material. Attempts to analyze the products were discontinued as impractical. This was based on the high cost of such analyses and the small amounts of material recovered.

RESULTS

The amounts of material recovered were small. In a run with sample II-B-9 no oil or tar was found in either of the water sprays. Any light fractions absorbed in the "Oleum Spirits" were very difficult to separate.

It was necessary to add 10 percent coal to several samples to secure burning. This agrees with previous findings (5) that roughly a calorific content of 600 Btu was necessary for combustion in the small return. When a sample of II-B-1 (425 Btu) was burned with 10 percent added coal nothing separated in spray No. 1, a "trace" separated in No. 2, and 3 ml in No. 3. Identical results were secured with II-B-9 (520 Btu) and a sample from the "Weldon mine" (calorific value not determined) run under similar conditions. This led to the suspicion that the material obtained came from the coal rather than the shale.

It is reasonable to assume that gaseous products would result from the partial combustion of the coal-like organic portion of the shale. It is this portion of the shale that accounts for the calorific value. Heating may cause the liberation of water from the inorganic portion. Sulfides might oxidize to form sulfur dioxide. If plenty of air were available the final combustion products would be expected to be carbon dioxide, water, and sulfur dioxide. Frush (5) gives the composition of smoke from one sample burned in the large retort as: CO , 0.7%; CO_2 , 1.4%; O_2 , 13.5%; H_2 , 1.8%; CH_4 , 0.7%; and N_2 , 81.9%.

The experimental results from the current work and that of Frush support the theoretical conclusion that little of value can be expected in the gases resulting from combustion of the shale. If sufficient organic material were available in the shale it is possible that part of it could be utilized to heat the shale and thus distill out the remainder. Frush points out that while combustion was supported in the large retort with shales containing as low as 360 Btu per pound that 1000 to 1500 Btu per pound was desirable for satisfactory burning. Most of the shales would not have sufficient calorific value to support combustion and have enough organic products left to utilize.

CONCLUSIONS

It was concluded that further work on this phase showed little promise and it was dropped to allow time and funds for more promising studies.

RECOVERY OF PRODUCTS FROM THE DESTRUCTIVE DISTILLATION OF SHALE

The shales being studied have characteristics similar to a very low grade bituminous coal. Coal has been destructively distilled for many years to give such products as coke, coal tar, light oils, and fuel gas. The coal tar is a source of many organic chemicals. The Iowa shales also have some resemblance to oil shale. Extensive research has shown that oil shale can be destructively distilled to produce gasoline and other fuel oils. Thus it seems reasonable to consider the possibility of useful products resulting from the destructive distillation of the Iowa shales under study.

In destructive distillation the shale is heated away from contact with air. Thus, while the constituents of the shale may change chemically, they would not oxidize and the possibility of degrading down to valueless products such as water and carbon dioxide is small. It is necessary to supply external heat which increases the expense of the operation.

ASSAYS BY THE MODIFIED FISCHER RETORT

Samples of the shales were assayed by the method developed by the U. S. Bureau of Mines (7). Shale ground to 8 mesh was heated in a modified Fischer retort (figure 4) at 500°C (932°F) for one hour out of contact with air. The distillate was recovered by condensing at 0°C and separating the oil and water in a centrifuge. Additional details on the

method are given in Appendix I. Results were calculated to gallons per ton of shale and are summarized in table IV. The distilled oil from Sample II-B-10 gave the results shown in table V.

LARGER SCALE STUDIES

The results secured with the Fischer retort indicated that greater yields of products should be secured by destructive distillation than with the partial combustion. This is to be expected. The partial combustion products were checked, since these would be the products from the initial studies on producing a road material. Two different retorts operated somewhat differently were used in these studies.

GAS FIRED RETORT

Equipment. The gas fired retort was a steel cylinder approximately four inches in diameter by eight inches long with a solid bottom and a flanged top. A discharge pipe led from the blind flange on the top to a water cooled condenser constructed of concentric pipes. The original condenser was found inadequate and replaced by two, each three feet long, operating in series. From the lower end of the second condenser the distillate ran either to a collecting bottle or to a graduated cylinder where the liquids separated. The gas then went to a 45 liter gas collecting bottle calibrated in 1 liter increments. Later four 18 liter gas collecting bottles were placed in series with the original bottle and a fiber glass filter was placed in the gas line between the liquid receiver and the gas collecting bottles.

The retort was heated by a large gas burner of the Bunsen type. Temperature was recorded on an automatic recorder using a thermocouple as the

sensing medium. A tee in the line to the first gas collecting bottle made it possible to supply gas to a Bunsen burner under a container of water used as a calorimeter (figures 5 and 6).

Procedure. A weighed shale sample was placed in the retort, and the top was bolted in place. The various parts of the assembly were connected. The gas burner was lighted, and the time was recorded. The automatic temperature recorder was started. The water to the condenser was turned on.

As the gas flowed from the distillate collection bottle (or graduated cylinder) to the gas collection bottle, the time was recorded for every five liters of water displaced to determine the rate of gas production. From this rate and the time the total gas produced was estimated. Gas in the excess of 45 liters was at first burned. After additional gas bottles were installed, the total volume was determined from actual displacement.

The heating value of the gas was obtained by burning a measured volume of gas under an insulated bucket containing a weighed amount of water. The calorific value was calculated from the weight of the water, the temperature rise, and the amount of gas burned. The results obtained in this determination were not as precise as those which might be secured by more conventional calorimeters. But it was believed that the accuracy was adequate for the purpose.

Originally the shale was ground to pass an 8 mesh screen and be retained on a 10 mesh screen. Since this size was considered rather small for practical utilization, runs were made using material passing a screen with 0.525-inch opening and retained on a screen with a 0.371-inch opening. The change in size made very little difference in results.

TABLE I. SHALE SAMPLE DATA*

Number	Origin	Cal. value Btu/lb	Analytical results in percentages					
			Moist.	Volatile	HCl Sol.	Silica	HF-residue	
II-B-1	Pershing Coal Co. pit	Marion Co.	425	0.5	9.4	9.9	56.8	23.5
II-B-2	Newton Mine pit	Marion Co.	1225	0.8	16.2	16.8	46.4	19.7
II-B-3	Newton Mine pit	Marion Co.	290	0.6	9.4	20.0	53.8	16.1
II-B-4	Newton Mine pit	Marion Co.	230	0.5	9.1	14.8	57.2	18.6
II-B-5	Patik Mine pit	Mahaska Co.	542	0.7	9.7	10.6	59.8	19.2
II-B-6	Jude Coal Co. pit	Marion Co.	940					
II-B-7	Engnes Mine pit	Mahaska Co.	790					
II-B-8	Angus Mine pit	Mahaska Co.	2075	2.7	21.9	17.9	40.4	17.2
II-B-9	Carbon Hill Mine pit	Mahaska Co.	520	2.9	12.3	7.7	39.3	37.8
II-B-10		Appanoose Co.	6050	1.2	43.3	18.7	23.0	13.8
II-B-11	Sunshine No. 4 mine	Appanoose Co.	4033	3.6	28.9	36.4	26.5	4.6
II-B-12	Sunshine No. 4 mine	Appanoose Co.	600	2.1	10.2	25.4	47.9	14.5
II-B-16	Pershing Coal Co. pit	Marion Co.	360					
II-B-18	Angus pit	Mahaska Co.	950					
II-B-20 ⁺	New Gladstone	Appanoose Co.						
II-B-21	Twin Coal Co.	Appanoose Co.						
II-B-22	Monitar Coal Co.	Appanoose Co.						
II-B-23	Appanoose Coal Co.	Appanoose Co.						
II-B-24	Weldon Mine							
II-B-25	McDaniel							
II-B-26	Farmington							

*II-B-1 to II-B-18 by Frush⁵.⁺Sample II-B-20 to II-B-23 were collected by the author near Centerville, Iowa.

TABLE II. RESULTS OF SCREEN ANALYSIS

Screen Mesh	Percentage passing		
	IIB9	IIB10	IIB15
6	99.9	100	100
8	98.9	98.6	98.8
10	71.4	64.4	70.8
14	49.0	43.2	51.3
20	34.2	29.4	38.7
28	24.6	20.9	30.8
35	17.9	14.8	24.8
48	12.9	10.5	20.6
65	9.2	7.4	17.5
100	6.6	5.4	15.4
150	4.4	3.7	13.4
200	3.1	2.7	11.8

TABLE III. SOXHLET EXTRACTION RESULTS

Solvent	Total extractables, wt percent		
	IIB9	IIB10	IIB15
Trichloroethylene	0.41	1.23	0.74
Hexane*	0.33	0.21	0.65
Benzol	0.26	0.72	0.37
Methylene chloride		0.81	
Perchloroethylene		0.69	

* "Skellysolve-B"

Time of extraction: methylene chloride and perchloroethylene, 4 hours; others, 2 hours.

TABLE IV. RESULTS OF SHALE ASSAYS BY THE MODIFIED FISCHER RETORT METHOD

Shale No.	Oil gal/ton	Water gal/ton
II-B-2	0.8	10.6
II-B-3	0.4	3.1
II-B-4	0.4	3.0
II-B-6	0.6	3.8
II-B-7	1.0	4.3
II-B-8	1.0	7.2
II-B-9	1.4	4.4
II-B-10*	23.2	5.5
II-B-12	0.7	3.4
II-B-14	0.5	3.4
II-B-15	0.3	2.4
II-B-16	1.3	2.2
II-B-24	0.6	1.4
II-B-25	0.3	1.5
II-B-26	0.2	0.6

* Average of four samples

TABLE V. DISTILLATION RESULTS

Oil from modified Fischer retort
Shale II-B-10

Distillate collected ml.	Temperature °C	Time min.
Fraction I		
0.05	87.5	
1.00	92.5	
2.00	123.5	
2.50	128.5	
3.00	135.0	
4.00	136.2	
Fraction II		
0.00	263.0	0.0
0.05	316.9	
0.38		1.0
0.60		2.0
0.78		3.0
0.95		4.0
1.00	336.0	
1.08		5.0
1.19		6.0
1.30		7.0
1.33		8.0
1.38		9.0
1.40		10.0
1.49		11.0
1.50	340.0	
1.55		12.0
1.62		13.0
1.68		14.0
1.75		15.0
1.80		16.0
1.82		17.0
1.82		18.0
1.90		19.0
1.90		20.0
1.92		21.0
1.98		22.0
1.98		23.0
2.00	346.0	24.0
Fraction III		
0.05	358.0	25.0
0.50	360.0	30.0
Out of thermometer range.		
Fraction IV		
0.00	352.2	0.0
0.05		0.0
1.00	393.9	10.0
1.50	396.6	15.5
2.00	404.5	17.0

Residue: viscous heavy oil, solidified on standing.

TABLE VI. DESTRUCTIVE DISTILLATION PRODUCTS FROM THE GAS-FIRED RETORT

No. Sample	Size*	Max. temp. °F	Distillate gal. per ton [†]	Gas Cu. ft. per ton	Btu per cu. ft.	Loss in weight %	
1	II-B-9	A	1600	20.1	520	12	
2	II-B-10	A	1640	34.8	3200	22	
3	II-B-11	A	1650	23.8	3600	420	19
4	II-B-20	C	1330	13.2	2000	470	15
5	II-B-20	D	1400	30.6	2600	480	22
6	II-B-21	D	1850	26.9	3000	380	21
7	II-B-21	D		24.8	4200	410	23
8	II-B-21	D	1500	30.6	2600	480	21
9	II-B-21	D	1400	23.8	2600	270	16
10	II-B-21	D	1400	28.0	2600	410	16
11	II-B-21	B	1400	27.5	2400	400	18
12	II-B-22	D	1550	27.5	3400	370	24
13	II-B-22	D	1630	25.9	3800	360	16
14	II-B-23	B	1600	29.6	3000	450	21
15	II-B-23	D	1650	18.0	3400	420	22
16	II-B-23	D	1670	22.0	3000	400	20
17	II-B-24	A	1500	13.2	600	0	5

*Sizes: A, through 3 mesh, on 8 mesh; B, 8 m, 10 m; C, 8 m, 20 m; D, through a 0.525" opening, on 0.371" opening.

[†]Total including both oil and water layers.

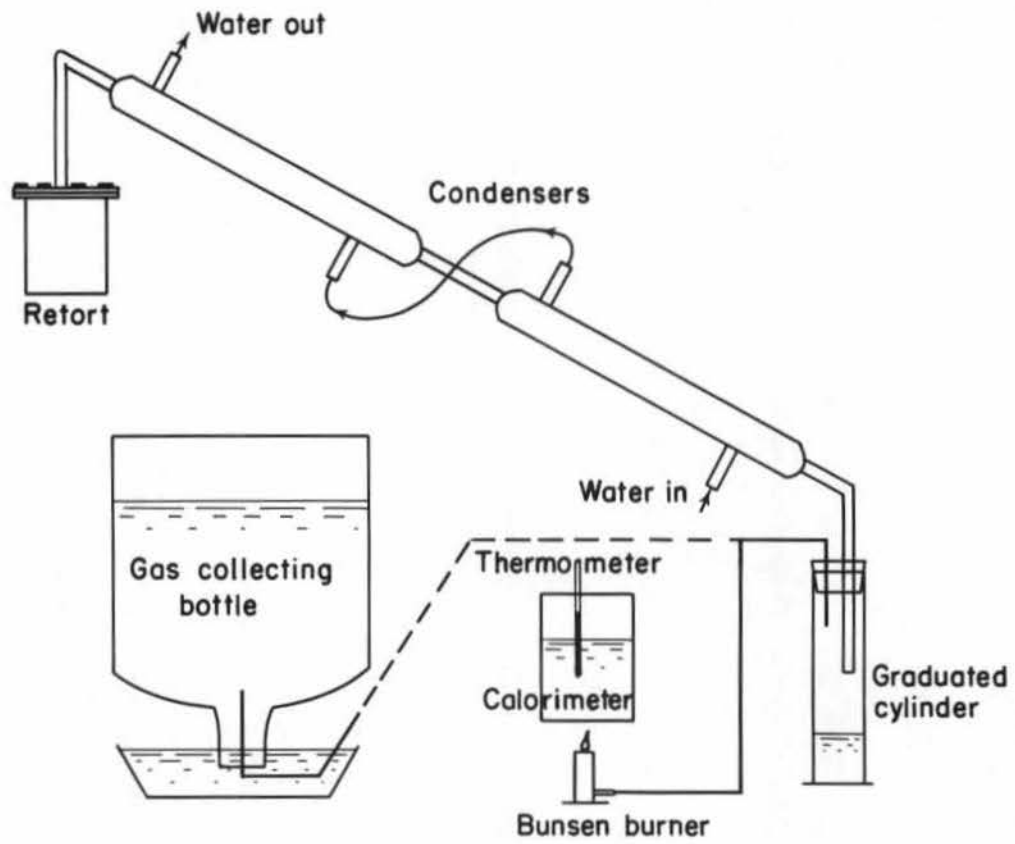


Fig. 5. Destructive distillation equipment.



Fig. 6. Destructive distillation equipment.

Results. Results are given in table VI. The distillate was distilled to give the boiling points of the fractions. Typical distillation results for No. II-B-10 shale are given in table VII. It was not deemed feasible to attempt analyses of the distillate fractions without the services of a good organic chemist. Further analytical work was dropped until the gas chromatographic equipment was available.

ELECTRICALLY HEATED RETORT

Purpose. The electrically heated retort was constructed to allow better control of the heating. Advantage was taken at this time of gas chromatography for analysis of the products. The equipment for gas chromatography was not available when the studies using the gas-fired retort were made.

Equipment. The retort (figure 7) was constructed of a 12.5 inch piece of 6 inch pipe fitted at either end with removable blind flanges or covers. It was heated by a winding of electrical resistance wire controlled by a variable transformer. It was provided with thermocouples for temperature measurement, a steam inlet, and gas and liquid outlets. Further details are given in Appendix II.

The equipment used for analysis was the "Model 500 Programmed Temperature Gas Chromatograph" manufactured by F and M Scientific Corporation of Wilmington, Delaware. The column was a copper tubing 15 feet long with an outside diameter of 1/4 inch. The packing was 25 percent by weight "Apiezon L" grease on fire brick particles sized from 65 to 35 mesh "Tyler Standard."

Experimental Procedure. A weighed sample of approximately 100 grams was placed in the retort. The retort was closed, and the liquid collector and entrainment trap were weighed and connected. The maximum current was

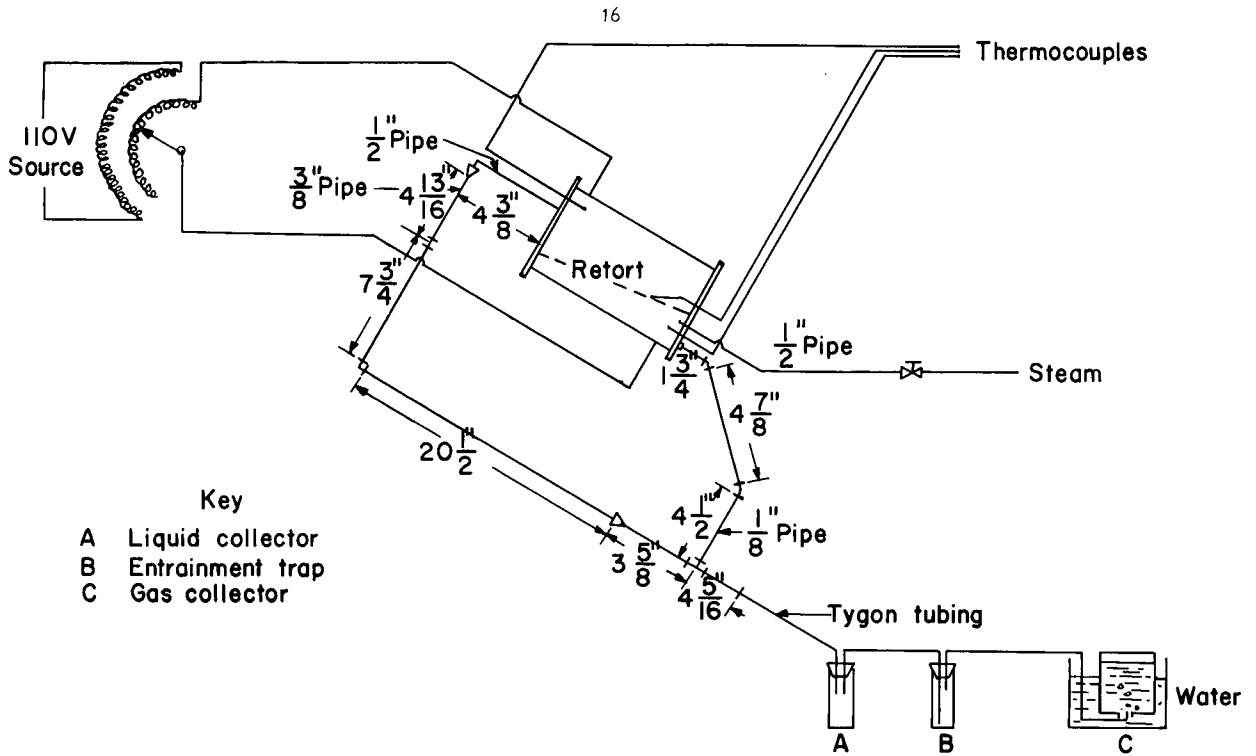


Fig. 7. Electrically heated retort.

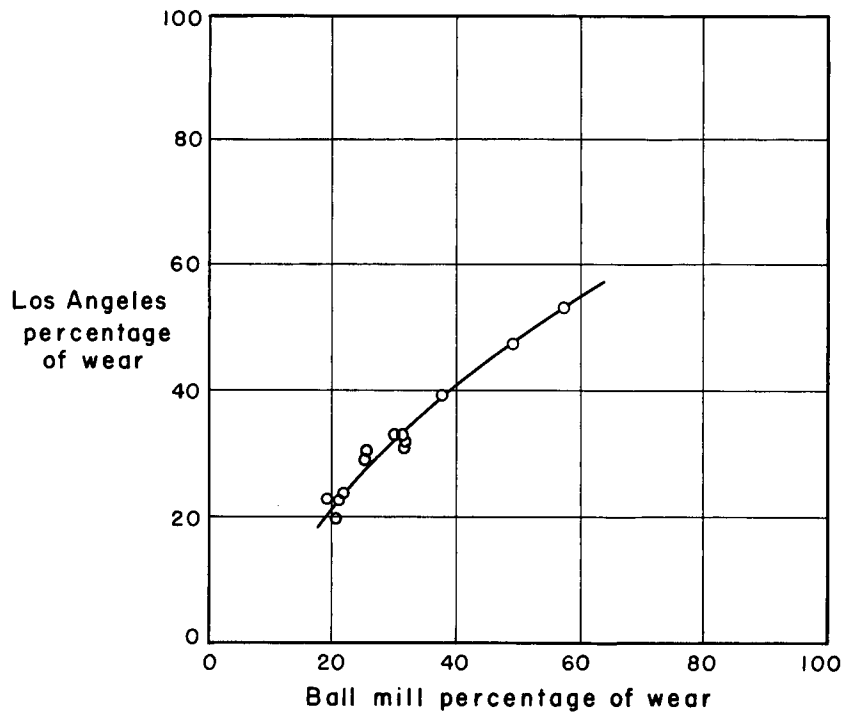


Fig. 8. Relationship between the Los Angeles abrasion tests and ball mill abrasion tests.

turned on. Temperature readings were taken at frequent intervals until a constant temperature was reached. Two runs were made with each sample, one without steam and one with steam injection. Steam injection reduces the amount of unsaturates, although it may increase nitrogen containing compounds. The maximum temperature was in the range of 800^o to 1000^oF and the time from 40 to 55 hours. Details of the procedure are given in Appendix III with time temperature curves (figures 14 to 19). The specific gravity of the samples and the amounts of gas and oil produced were determined (table VIII). The composition of the liquid (oil) was determined by gas chromatography. A detailed discussion of the analytical methods is given in Appendix IV.

Results. Both gas and a liquid were collected (table VIII). The liquid had two layers of immiscible solutions: a brownish colored one on the bottom, and a black one on the top. When steam was added, the brownish colored layer increased in volume. It was assumed that the brownish layer was mainly water. The oil fractions (black liquid) were analyzed (table IX). Apparently the steam caused some minor cracking of the oil.

RESIDUE STUDIES

Frush (5) used a modification of the "Los Angeles Abrasion Test" (ASTM-C 131-46; AASHO-T96-46) to evaluate the hardness of the burned shale. The Los Angeles method requires 5000 grams of feed. He reduced the amount to 500 grams and ran the samples in a laboratory ball mill. The relationship between results by this method and the standard method are shown in figure 8. Details of the test are given in Appendix V.

The abrasion test was applied to the shale residues from the gas fired retort runs listed in table VI. The results are summarized in tables X, XI.

Three naturally burned shale showed the following abrasion: 16.25%, 52.7%, and 84.0%.

Water absorption of the heat treated shale was determined by first allowing the sample to soak overnight in water and then allowing the surface to dry. The sample was then dried at 70°C in a drying oven, and the moisture loss was calculated as a percentage of the dry weight of the sample (table IX). Two naturally burned shales showed absorptions of 11.1% and 12.8%. A third disintegrated to a mud. In a second procedure the sample, after soaking overnight, was centrifuged from two to eight minutes (table XII). Most determinations were made by centrifuging two minutes. Comparative data for a II-B-10 destructively distilled sample is as follows: 2 minutes, 20.6%; 4 minutes, 20.3%; 6 minutes, 19.9%; and 8 minutes, 18.0%.

DISCUSSION

The objectives of the original shale project was to produce a material suitable for use in road building. The shale consists of both inorganic and organic constituents. The inorganic portion of the shale needs heat treatment to produce a material suitable for road use. The organic portion of some of the shales has a high enough fuel value that it may be used to furnish the necessary heat treatment by a simple process of burning the shale. However, in general the shales do not appear to have a high enough organic content to produce the necessary heat both to process them into road building materials and in addition to supply amounts of organic by-products worth recovering.

The maximum amount of organic by-products was obtained by heating the shale out of contact with air. The composition of the by-product material obtained by this destructive distillation process depended in part upon

TABLE VII. DISTILLATION RESULTS

Gas fired retort at 1350°F. Shale II-B-10

Distillate collected, ml.	Temperature °C
0.1	94.5
10.0	100.2
20.0	109.8
30.0	110.3
40.0	112.0
50.0	115.0

Oil bumped vigorously resulting in some loss. Distillation was resumed.

50.1	225.5
51.9	269.4
52.0	272.8
52.5	279.1
53.0	280.3
53.5	281.4
54.0	283.1
54.5	284.7
55.0	295.8
55.5	296.3
56.0	302.4
56.5	304.5
57.0	306.7
57.5	308.9
58.0	312.2
58.5	315.0
59.0	316.7
59.5	320.0
60.0	320.6
60.5	327.8
61.0	328.9
61.5	333.3
62.0	335.0
62.5	337.8
63.0	340.0
63.5	342.2
64.0	343.9
64.5	346.1
65.0	346.7
65.5	347.8
66.0	348.9
66.5	349.4
67.0	350.0
67.5	350.0
68.0	350.0
68.5	358.0

Total at start: 118 ml.

TABLE X. MODIFIED ABRASION TEST RESULTS

Run No.	Sample	Abrasive wear in percent	
		As determined	Equivalent L.A. value
1	II-B-9	28.1	37.0
2	II-B-10	39.6	48.0
3	II-B-11	37.6	46.0
4	II-B-20	70.6	86.0
6	II-B-21	54.3	67.0
14	II-B-23	65.8	80.0
15	II-B-23	62.9	76.0
17	II-B-24	35.7	45.1

Note: Run numbers correspond to those in table V.

TABLE XI. MODIFIED ABRASION AND ABSORPTION TEST RESULTS—BURNED SHALE

Sample	Burning temp. °F	Modified abrasion test, % wear	Water absorption, %
II-B-6	1800	26.5	9.7 (9.2)
II-B-7	1200	38.4	13.4
II-B-9	1400	26.5	9.0 (8.8)(8.9)
II-B-14	1800	20.6	9.8 (6.6)(9.4)
II-B-16	1800	38.1	11.8
II-B-24		30.3	13.6

Note: Absorption values in parentheses lack burning temperature data.

TABLE VIII. OIL PRODUCED IN THE ELECTRICALLY HEATED RETORT

Sample	Gr. per gr. sample	Lb. per ton sample	Gal. * per ton
II-B-2	0.056	112	16.0
II-B-10	0.122	244	39.9
II-B-20	0.089	178	25.4
II-B-21	0.111	222	31.7
II-B-22	0.130	260	37.1
II-B-23	0.141	282	40.3

* Estimated from an assumed weight of 7.0 pounds per gallon, average.

TABLE IX. COMPOSITION OF VARIOUS OIL SAMPLES*

Sample	Without steam injection		Weight percent †	With steam injection	
					Weight percent
II-B-2	Isopentane		99.6	Pentadiene-1,3	59.8
	Pentane		T	Cyclopentane	0.3
	Pentadiene-2,3		0.2	Isopropyl acetate	29.5
	Pentadiene-1,3		T	3-Ethyl-pentane	T
	Cyclopentane		0.1	Butanol-2	T
	3-Methyl-hexane		T	2,2,3,3-Tetramethyl-butane	T
	3-Ethyl-pentane		T	Methyl-benzene	9.3
	2-Methyl-butanol-2		T	Pentanol	0.7
	Pentanol-3		0.1		
	1,2-Dimethyl-benzene		0.1		
II-B-10	Butyne-1		0.1	Butyne-1	0.1
	2-Methyl-butane		9.2	Pentene-1	33.3
	Pentene-1		89.4	Pentane	63.3
	2-Methyl-butanol-2		0.9	Pentadiene-2,3	T
	2,2-Dimethyl-propanol-1		T	Pentadiene-1,3	T
	Pentanol-2		T	Cyclopentane	T
	2-Methyl-butanol-1		0.1	3-Ethyl-pentane	T
	1,3,4,5-Tetramethyl-benzene		0.2	n-Heptane	T
	2,4,6-Trimethyl-phenol		0.1	2-Methyl-butanol-2	3.2
				Pentanal	T
II-B-20	Butyne-1		0.2	1,3-Dimethyl-benzene	0.1
	Ethyl nitrite		0.1		
	Pentadiene-1,3		88.2	Butyne-1	0.1
	2-Methyl-hexane		3.4	Pentane	93.7
	Methyl-benzene		6.1	Pentadiene-2,3	0.8
	Pentanol-2		1.8	Pentadiene-1,3	1.3
	Isopropyl benzene		0.2	Propanol-2	1.0
				2-Methyl-hexane	T
				3-Ethyl-pentane	T
				Pentanal	0.1
II-B-21	Pentane		49.8	2,2,3,3-Tetramethyl-butane	2.7
	Pentadiene-1,3		41.9	2,2-Dimethyl-propanol-1	0.3
	3-Ethyl-pentane		5.2		
	2,2,3,3-Tetramethyl-butane		2.2		
	Pentanol-3		0.9		
II-B-22	Ethyl nitrite		0.1	Ethyl nitrite	0.1
	Pentene-1		84.1	Pentane-1	0.4
	Pentadiene-1,3		11.5	Pentane	96.5
	Cyclopentane		0.1	Pentadiene-1,3	0.1
	Propanol-2		4.5	Cyclopentane	0.1
	Methyl-benzene		0.4	2-Methyl-hexane	T
	1-Methyl-2-ethyl-benzene		0.1	Methyl-benzene	2.8
	1-Methyl-4-isopropyl benzene		0.1		
				Ethyl nitrite	0.6
				Pentadiene-1,3	96.8
II-B-23	Ethyl nitrite		0.1	Isopropyl acetate	T
	Pentadiene-2,3		97.6	n-Propyl alcohol	1.3
	3-Ethyl-pentane		T	2,2,3,3-Tetramethyl-butane	1.3
	2-Methyl-butanol-2		0.4		
	2,2,3,3-Tetramethyl-butane		0.1	Ethyl nitrite	0.2
	Methyl-benzene		1.4	Pentene-1	96.2
	Pentanol-2		T	Pentadiene-2,3	T
	2,4-Dimethyl-heptane		0.2	Cyclopentane	0.1
	1,2,3,4-Tetrahydro-naphthalene		0.1	3-Methyl-hexane	T
	Naphthalene		0.1	2,2,3,3-Tetramethyl-butane	2.4
			Methyl-benzene	0.8	
			1,2-Dimethyl-benzene	0.1	
			1-Methyl-2-isopropyl benzene	0.2	

*The components are listed in the order of increasing boiling points.
† Denotes trace quantities only.

TABLE XII. WATER ABSORPTION—CENTRIFUGE METHOD

Sample	Treatment	Absorption, %
II-B-1	D.D.	8.8
II-B-9	Burned	9.9
II-B-10	D.D.	20.6
II-B-11	D.D.	16.7
II-B-11	D.D.	16.9
II-B-16	D.D.	9.6
II-B-16	Burned	12.6
II-B-20	D.D.	14.1
II-B-20	D.D.	14.7
II-B-23	D.D.	23.1
II-B-23	D.D.	20.7
II-B-23	D.D.	22.8
II-B-24	D.D.	8.7
II-B-24	Burned	4.0

D. D. indicates "Destructively Distilled".

the temperatures used in the process. At temperatures between 800 and 1000°F used in the electrically heated retort the main products were pentane, isopentane, pentene-1, pentadiene 1, 3, and pentadiene 2, 3. If these products had been present in the original shale they would have been extracted in early studies when hexane, benzol, trichloroethylene, methylene chloride, and perchloroethylene were used as solvents. Since only a negligible amount of anything was extracted, we may assume that a considerable amount of thermal breakdown occurred in the retort.

The product from the Fischer retort was not analyzed. It had a higher boiling range than the mixture of products from the electrically heated retort would have. The liquid product from the gas fired retort at 1350°F was not analyzed. It had a higher boiling range than that from the electrically heated retort. The products formed at two different temperatures would be expected to differ. The product from the Fischer retort resembled that from the gas fired retort, although it was produced at a temperature closer to that used in the electrically heated retort. Differences in rate of heating may account for some of this apparent lack of agreement.

It is difficult to make a realistic evaluation of the products since most of these have a limited market. The sample II-B-2 yielded the equivalent of 21.6 gallons per ton of isopentane. Isopentane sells currently at about 40 cents a gallon or a total value of \$8.64 per ton of shale. The product from II-B-21 is about one half pentane worth, at 14 cents a gallon, approximately \$2.91 per ton of the shale. The other principal constituent is pentadiene 1, 3 currently quoted at \$2.75 a gallon. This is equivalent to \$44.00 a ton. The principal product from II-B-10 is pentene-1 (propylethylene or *A*, *n* amylene). The yield was 40.5 gallons per ton. This is quoted at \$12.50 per 100 grams but obviously would sell for only a fraction

of this for industrial use. No attempt has been made to calculate the cost of separation and purification of the various compounds.

No data were obtained on the amount of heat required in the destructive distillation when gas was used as a fuel. The amount of electricity used for heating gives a heating value obviously unrealistic. Frush (5) reports good burning with 1000 to 1500 Btu per pound. It might be possible to heat the retort by burning shale and supplement it with the gas from the retort. The residue from both burning and distillation would be available for road use. Only the better shales, such as II-B-10 with a calorific value of 6050 Btu, would offer promise.

SUMMARY AND CONCLUSIONS

Bituminous shale from Iowa coal fields were extracted by various solvents with no significant results. The by-products from the burning of the shale appeared to be of little or no value. The products from destructive distillation in a Fischer retort and a larger gas fired retort were not analyzed. The products from destructive distillation in an electrically heated retort were analyzed by gas chromatography. Principal constituents were isopentane, pentane-1, butadiene-1, 3, pentane, and pentadiene,-2,3.

Insufficient data are available for appraisal of possibilities. The analytical data secured by gas chromatography were determined from a benzene extract of the original sample and should be checked. Destructive distillations should be carried out at other temperatures. A combination of burning and destructive distillation needs study. Further tests on the residual solid material are needed.

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Standard Method for the Assay of Oil Shale by the Modified Fischer Retort. Laramie, Wyoming. November 1948.

APPENDIX I.

METHOD OF ASSAYING OIL SHALE BY A MODIFIED FISCHER RETORTAPPARATUS

The apparatus used was the following: A cast aluminum retort (figure 9) with a heat insulating shield and equipped with a pyrometer reading to 500°C; an Allihn-type glass condenser, a 100 ml graduated centrifuge tube, and a glass adapter for connecting (figure 10); a 400 ml beaker used as a cooling bath; a Meeker type gas burner; a suitable support (figure 10).

PROCEDURE

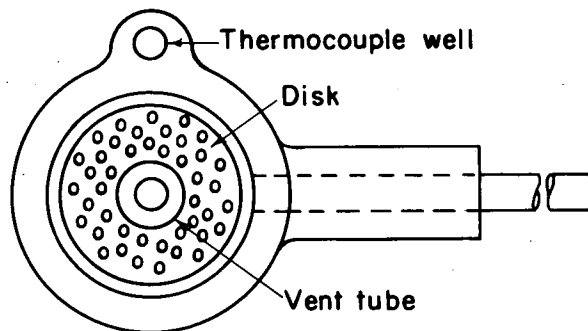
A 100 gram sample of shale crushed and screened to 8 mesh and dried for one hour at 105°C was placed in the retort and the apparatus was assembled. The retort was heated at 500 \pm 5°C until all distillate had come over (normally about 60 minutes). The centrifuge tube and contents were weighed after coming to room temperature and then were centrifuged to cause the contents to separate into two layers. The volume of water in milliliters was reported as the weight in grams. Specific gravity of the oil was determined by pipetting a known volume and weighing.

The yields of oil and water are calculated by the following formula:

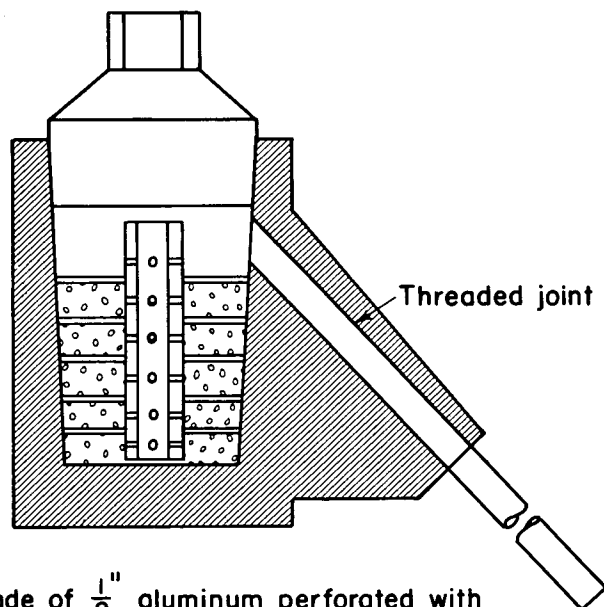
$$\begin{aligned} & \text{Gallons of oil (or water) per ton of shale} \\ & = \frac{\text{Milliliters of oil (or water)} \times 239.7}{\text{Grams of shale}} \end{aligned}$$

The above method has been condensed, and the figures are copied directly from "Bureau of Mines Report of Investigations 4477." June 1949. (7)

Top view with plug removed



Cross section of retort



Disks made of $\frac{1}{8}$ " aluminum perforated with numerous $\frac{3}{32}$ " holes.

Vent tube made of $\frac{3}{4}$ " aluminum with $\frac{3}{8}$ " center and numerous $\frac{3}{32}$ " holes.

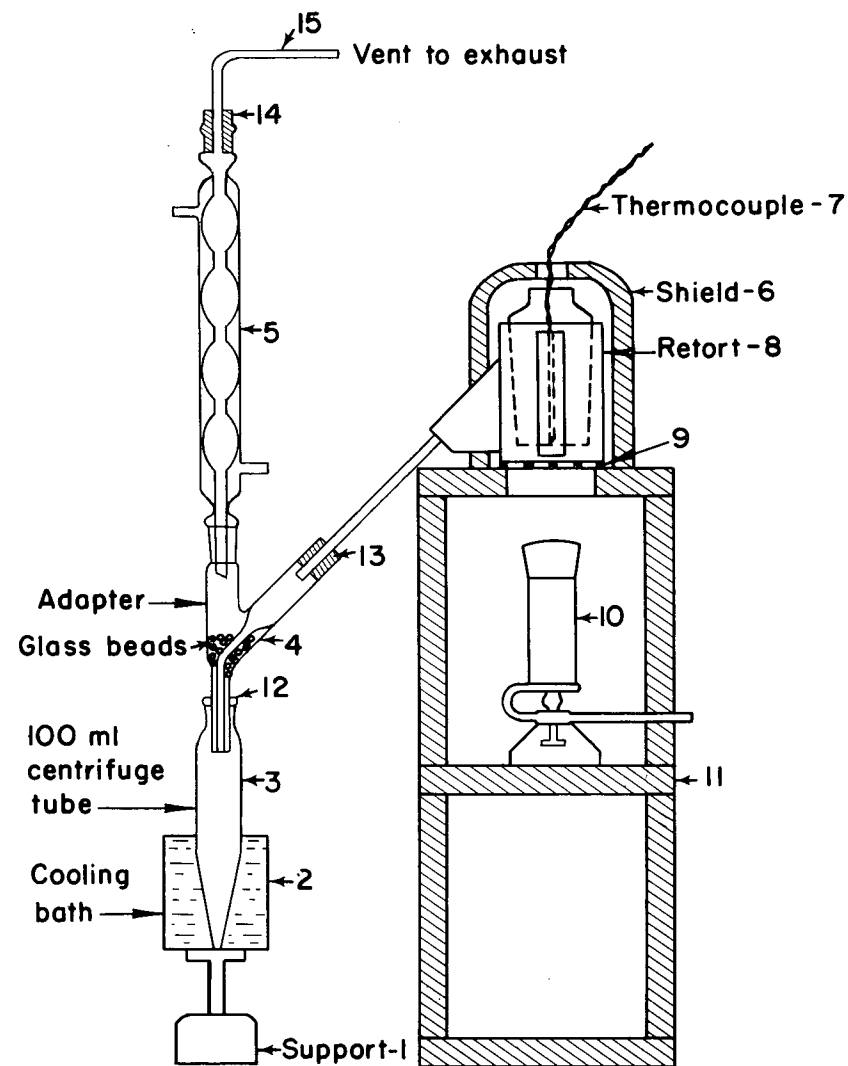


Fig. 9, at left. Modified Fischer retort charged with oil shale.

Fig. 10, above. Oil shale retorting unit.

APPENDIX II *

ELECTRICALLY HEATED RETORT

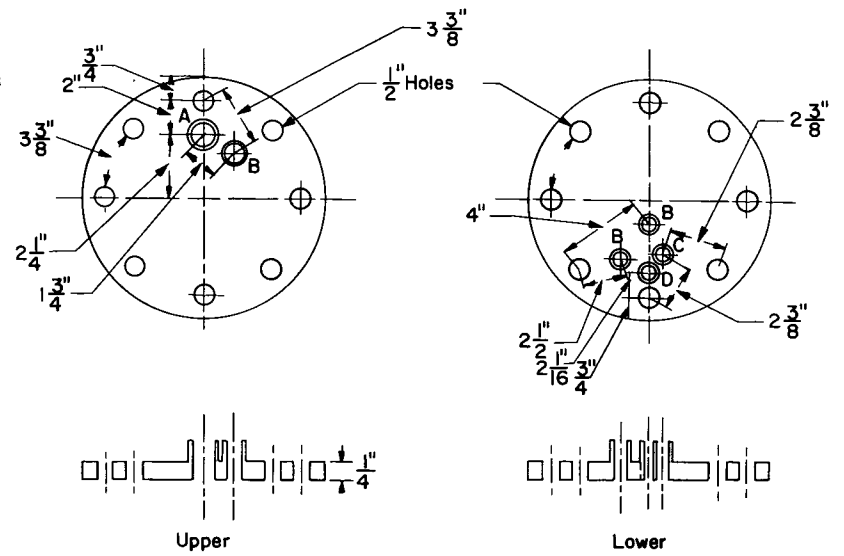
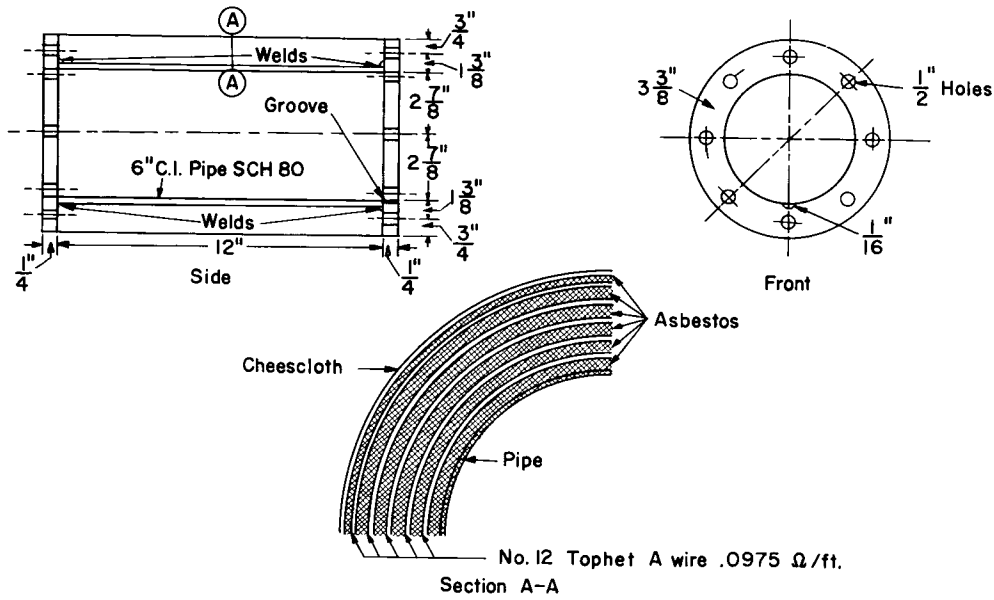
The retort (figures 11, 12, and 13) was a schedule 80 steel pipe 12 1/2 inches long with flanges and an inside diameter of 5.761 inches. On the bottom of the front or lower end of the retort was a 1/16 inch deep groove approximately 2 inches in length. The covers were made of 1/4 inch thick steel plates 5 inches in radius, and each was connected to the retort with 8 bolts having 1/2 inch diameters with nuts and washers.

The lower or front cover had two thermocouple entrances. One was immediately above the false bottom with the thermocouple at least six inches within the retort. The second was approximately one-half inch within the retort near the drip or liquid outlet. The drip was 2 3/16 inches from the center of the cover. A one-half inch nipple welded near the drip opposite of the thermocouple entrance allowed for steam insertion. This fitting was lower than the false bottom. All other fittings were one-quarter inch nipples welded to the cover.

The upper or back plate had a 1/2 inch nipple welded 2 1/4 inches from the center. One and one-quarter inches away was a thermocouple entrance consisting of a 1/4 inch nipple welded to the cover. The thermocouple was about one-half inch within the retort.

Iron-constantan thermocouples were used. The thermocouples were sealed with a mixture of asbestos and sodium silicate. A thin ring of asbestos was used as a gasket. Both covers had a half-inch layer of asbestos.

*Information in the Appendices II to IV has been copied directly from the thesis by LaRose (6).



- Key**
- A Gas outlet, $\frac{1}{2}$ " nipple welded
 - B Thermocouple well, $\frac{1}{4}$ " nipple welded
 - C Steam inlet, $\frac{1}{2}$ " nipple welded
 - D Drip (liquid outlet), $\frac{1}{4}$ " nipple welded

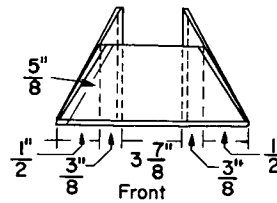
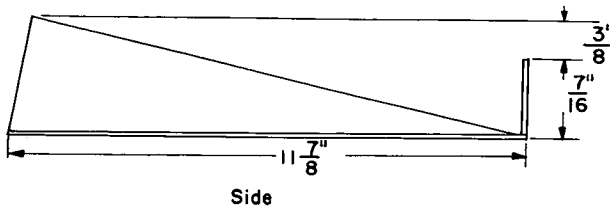
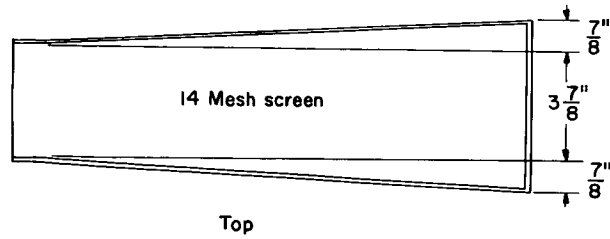


Fig. 11, at left, above. Retort details.

Fig. 12, above. Retort covers.

Fig. 13, at left. Shale support.

The heating element was 100 feet of Tophet A (Nichrome IV) wire with a diameter of 0.081 inch (American or Brown & Sharpe Gage Number 12) with a resistance of 0.0975 ohms per foot donated by the Wilbur B. Driver Co., Newark 4, N. J. Asbestos was used as a filler to prevent short circuits or groundings. Then a layer of asbestos was applied for insulation with a covering of cheese cloth. The overall thickness was two inches. The high resistance wire was connected to a variable transformer with a capacity of 20 amperes. The 16 bolts were sealed into place with their heads in the asbestos layer.

The false bottom (figure 13) was made from a 14 mesh screen and was 11 7/8 inches in length with a front piece of 7/16 inch in height to prevent spillage. The sides were 13/16 inch in height at the back and tapered to zero at the front. The width was 3 7/8 inches at the back and 5 5/8 inches in front. The retort was supported on a steel stand at approximately 23° from the horizontal.

A series of fittings and pipes were used to connect gas and liquid outlets together. This line was not insulated allowing it to act as a condenser. A piece of "Tygon" tubing ran from a tee in the line to a glass liquid collector. Another piece of "Tygon" tubing ran from the liquid collector to a flask that acted as an entrainment trap. A third piece of the "Tygon" tubing ran from the entrainment trap to a gas collector. Gas was collected by the displacement of water. During runs using steam a five gallon glass jug filled with water was used as the gas collector. For the other runs a sample jar filled with approximately 500 milliliters of water was used. All stoppers were made of cork.

APPENDIX III

EXPERIMENTAL PROCEDURE

The front cover was bolted on with an asbestos gasket in place and was not removed except for cleaning.

The empty false bottom was weighed. Approximately 100 grams of sample were placed and spread on the false bottom and weighed. The false bottom was then placed into the retort with the front piece against the front cover. The two thermocouples of the front cover were separated by the false bottom. The long top thermocouple was bent, and the tip was inserted into the bed. The rear gasket was put into place, and the rear cover was bolted on. The line for the two outlets was closed by a union in the line near the rear cover. The liquid collector and entrainment trap with their final covers were weighed. The tubings were put into place. The specific gravity of the sample was taken.

The variable transformer was turned on to 95 percent of the maximum amperage output. Frequent temperature recordings were needed during the first run to prove that the temperature did reach an equilibrium and remained constant. After that temperature readings were taken frequently until the temperature reached equilibrium. Then the temperatures were recorded occasionally for checking.

Two runs were made with each sample, one without steam and one with steam injection. For the run without steam injection the run was terminated after approximately 55 hours of operation. For the run with steam injection, the steam valve was opened approximately 15 hours after equilibrium had been reached. The run terminated when either the liquid collector or gas collector was filled.

When the run terminated, a clamp was placed on the tubing connecting the liquid collector and the outlet line. The tubing was then removed from the outlet line, and the variable transformer was turned off. Volumes of liquid and gas collected were recorded. All three containers were then stoppered. The liquid collector and entrainment trap were again weighed. The liquid in the entrainment trap was poured into the liquid collector, and the liquid collector was sealed air tight.

The retort was cool enough to handle after eight hours of standing. The union near the rear cover was uncoupled, and the rear cover was removed. The thermocouple was lifted up from the sample, and the false bottom was taken out and weighed. The specific gravity of the sample was taken. The sample was then discarded.

Time-temperature curves for the various runs are shown in figures 14 to 19.

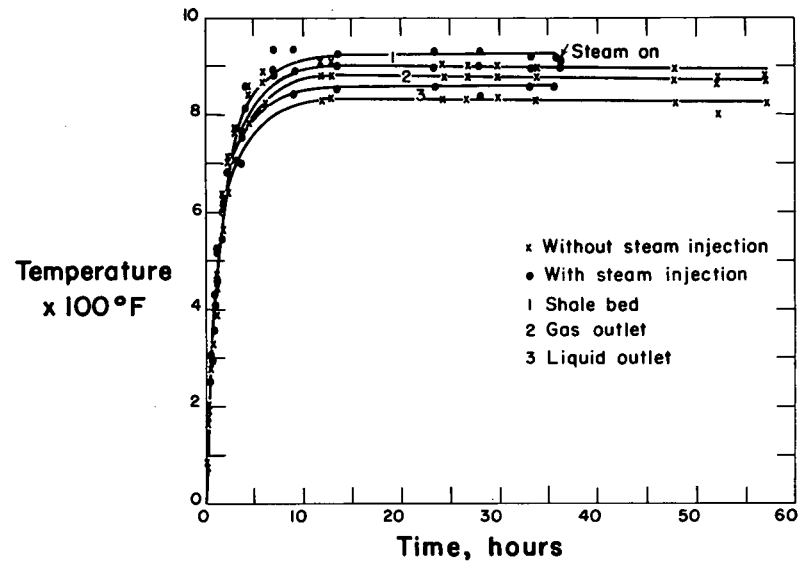
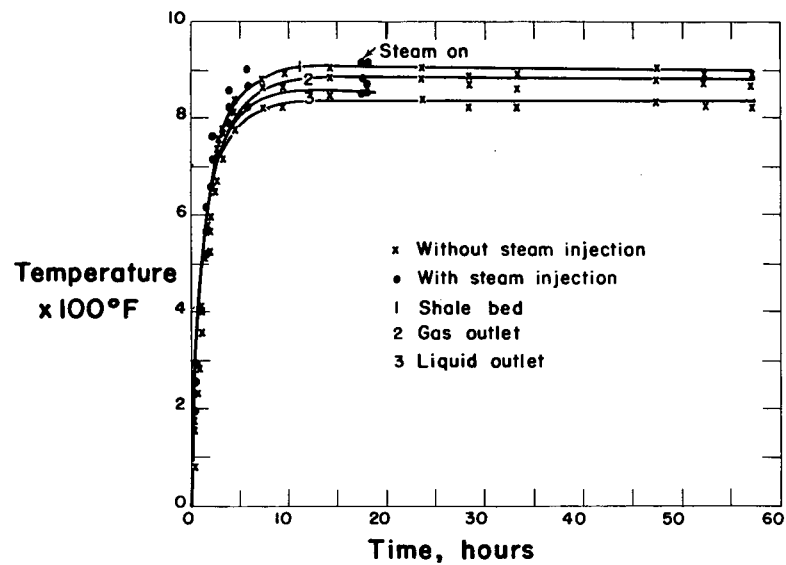


Fig. 14, at left, above. Temperature distribution in the retort during operation with sample II-B-2.

Fig. 15, above. Temperature distribution in the retort during operation with sample II-B-10.

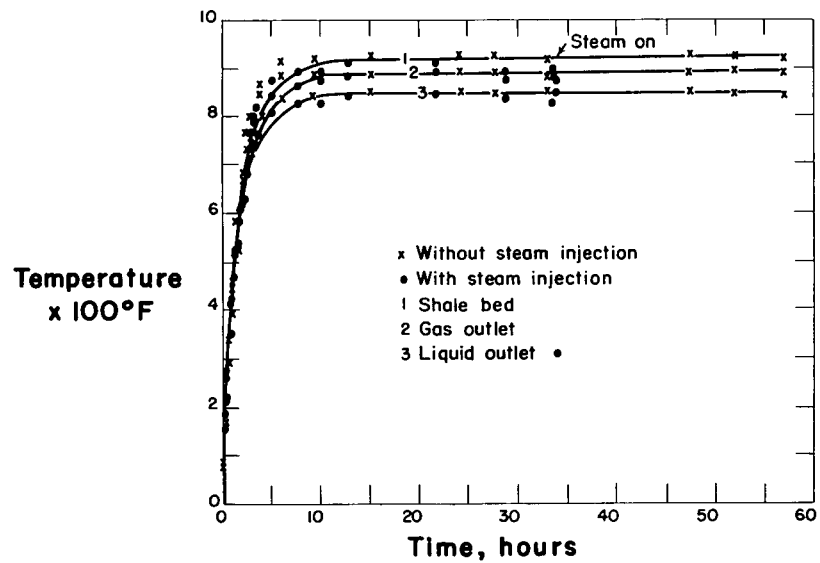


Fig. 16, at left. Temperature distribution in the retort during operation with sample II-B-20.

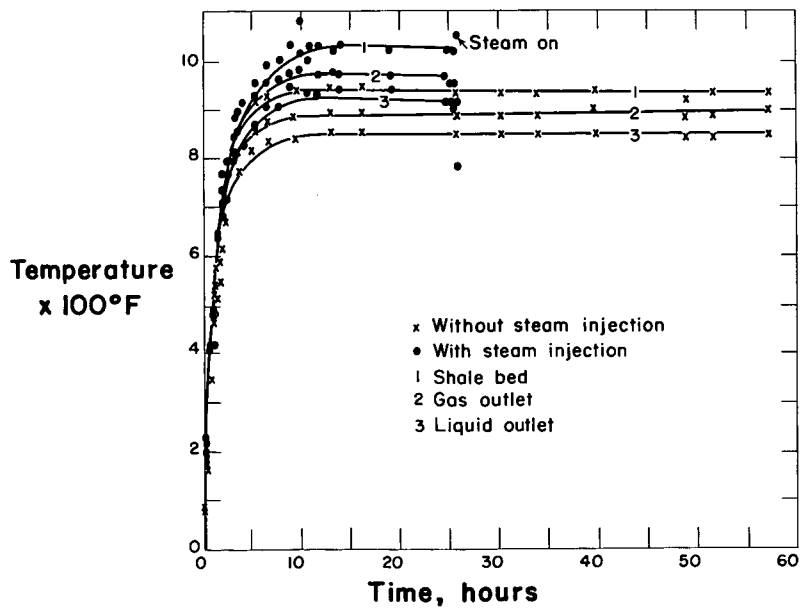
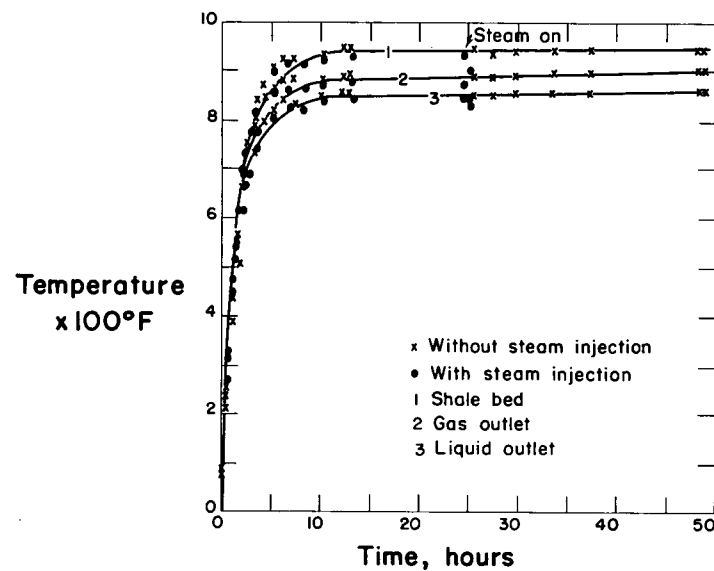
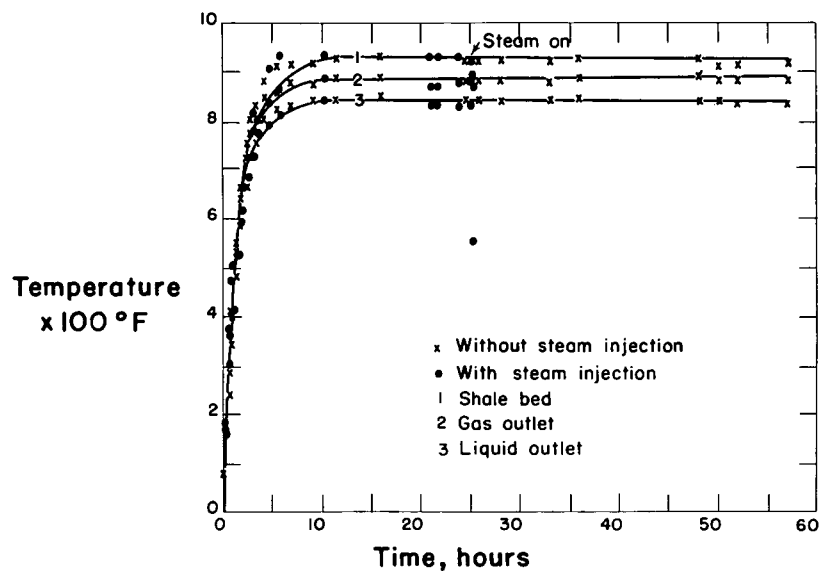


Fig. 17, at left, above. Temperature distribution in the retort during operation with sample II-B-21.

Fig. 18, above. Temperature distribution in the retort during operation with sample II-B-22.

Fig. 19, at left. Temperature distribution in the retort during operation with sample II-B-23.

APPENDIX IV.

ANALYTICAL PROCEDURESAMPLE PREPARATION

The oil obtained from the shale contained a large amount of water. Water is difficult to analyze by gas chromatography, but removal might upset the quantitative analysis of the original sample. Leaving the water in the sample might confuse the recording of the analysis by distorting peaks of other constituents. It was decided to remove the water and place the emphasis of the analysis on qualitative results.

Benzene was added to the sample, and the mixture was thoroughly shaken. Benzene was chosen as solvent because most organic compounds are soluble in benzene, and water is only very slightly soluble in benzene. The mixture was allowed to stand until two layers appeared; the benzene solution layer was on top. One hundred microliters of the benzene solution was placed in a vial, and ten microliters of chloroform was added as an internal standard. Densities of chloroform and solution were taken before they were added. The vials were sealed air tight.

The samples were prepared shortly before they were to be used.

PACKING AND COLUMN PREPARATION

The packing was 25 percent "Apiezon L" grease on from 65 to 32 mesh fire brick (1). The fire brick was first crushed in a hammer mill with a 1/8 inch screen and then in a 6 inch roll mill. This product was then separated into size fractions. The desired fraction was removed and placed in a beaker. Then the fraction was washed with tap water, stirred vigorously, allowed to settle, and the fines were poured out with the water. This was done ten times. Then the fraction was washed in the same manner for five times

using hydrochloric acid with one and a half volumes of acid to one volume of fire brick. Finally, the fraction was dried overnight in a vacuum oven at 100°C.

Twelve and one half grams of "Apiezon L" grease was weighed in a large beaker. Chloroform was added slowly to dissolve the grease. This required from 300 to 400 milliliters of chloroform. To this solution was added 37 1/2 grams of the freshly prepared fire brick. The solvent was allowed to evaporate up to one half inch above the fire brick level. Then the mixture was stirred vigorously until the mixture was crumbly or appeared dry. This mixture was placed in a large watchglass and allowed to dry overnight in a vacuum oven. The mixture was again separated into size fractions. The final fraction was from 65 to 35 mesh "Tyler Standard."

A copper tubing with 1/4 inch outside diameter and 15 feet long was used for the column (1). An allowance of three-quarters inch on each end was made for insertion of an inert material to provide a false bottom to keep the packing enclosed.

One end of the tubing was sealed with tape to prevent packing from falling out while being packed. The packing was poured into the tubing. A vibrator was used to pack the material as tightly as possible. Approximately 45 grams was used. After the column was completely filled, the other end of the tubing was taped. The column was coiled and bent to fit into a removable oven within the apparatus. The ends were now untaped. Three-quarters inch of packing was removed from each end. This space was packed with spun glass ("Angel hair"). The proper fittings were installed, and the column was fastened into the gas chromatography system. The oven was put into place. The system was ready for operation.

PROCEDURE

Maximum sensitivity range was used. The oven was turned on with a thermostat setting of 150°C. The thermal conductivity cell was at 200°C. The injection port was also maintained at 200°C. Maximum helium flow rate was used with a pressure of 17 pounds per square inch; this flow rate was approximately 55 milliliters of helium per minute. The speed of the chart was at its minimum. It took approximately an hour for equilibrium to be reached and the base line to be constant on the recorder.

One hundred microliters of sample was injected into the system. The time of injection was marked on the recorder. A close watch was maintained on the recorder. If any peaks went beyond the range of the recorder, the sensitivity was reduced proportionately until it could be safely increased again. The runs were two hours long.

The correlation between relative retention times and boiling points used for identifying the constituents is shown in figure 20.

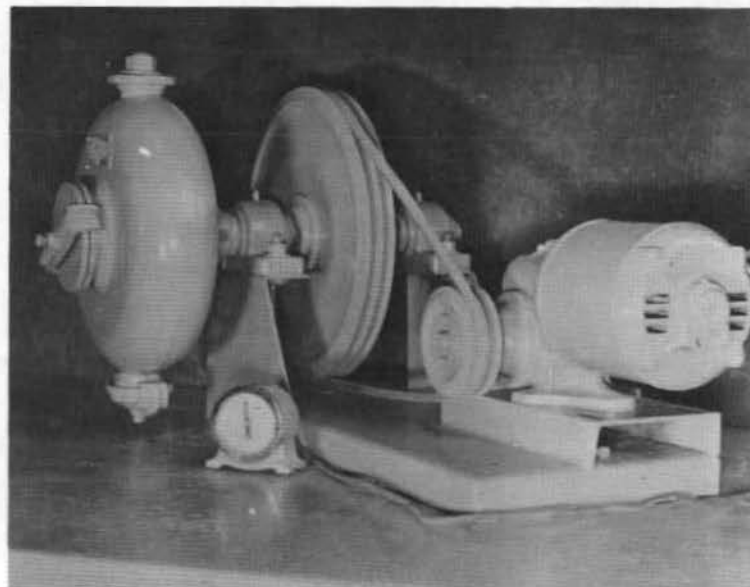
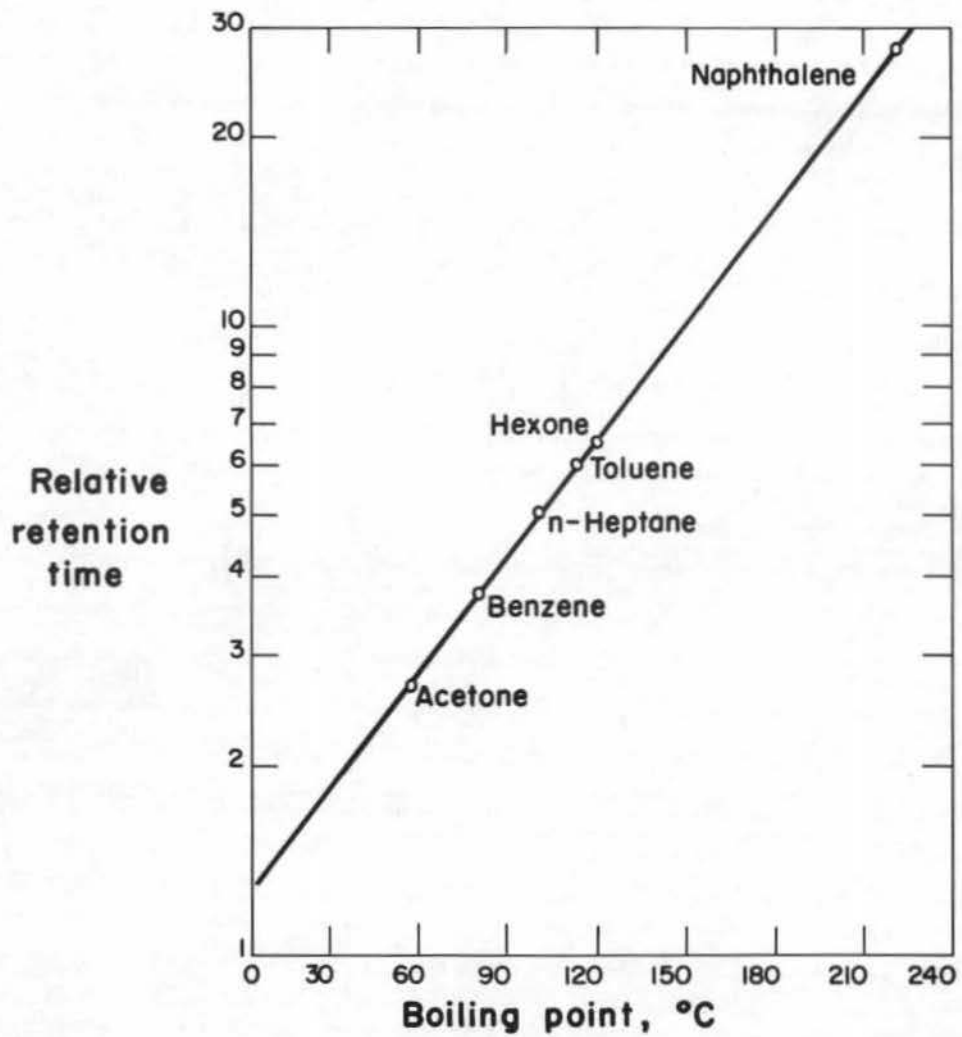


Fig. 20, at left. Correlation between relative retention time and boiling point for gas chromatography results.

Fig. 21, above. Ball mill used in abrasion tests.

APPENDIX V

BALL MILL ABRASION TEST

The ball mill used is of the closed laboratory type, 16 inches in diameter and 4 inches wide. The outer rim is toroidal. A semi-circular shelf is fastened on the inside periphery to elevate the two 500 gram steel balls used for producing the impact and abrasion. The mill was rotated at 18 revolutions per minute, this time having been found to produce results most similar to those of the standard Los Angeles test. A photograph of the mill is shown in figure 21.

In use 500 grams of feed, graded to pass a No. 4 U.S. standard sieve and to be retained on a No. 8 sieve, was placed in the mill with the two balls. A calibrated timer was set for exactly 18 minutes and the mill was started. At the end of the period the mill stopped and the sample was removed and screened. That percentage not retained on a No. 12 sieve (1680 microns) was termed the percentage of wear. This value may be converted into equivalent Los Angeles test values by reference to the curve, which was developed from the testing of a number of samples by both methods.