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Destructive Distillation Products of Certain Iowa Carbonaceous Shales

LIONEL K. ARNOLD¹

Abstract. Modified Fischer retort assays resulted in up to 23.2 gallons of oil per ton of shale from carbonaceous shales from southern Iowa coal fields. Destructive distillation was also carried out in two different laboratory retorts. Yields of an oily liquid up to 39.9 gallons per ton were secured. Analyses showed one sample consisting of 89.4 per cent pentene-1 and 9.2 per cent 2-methyl butane with minor amounts of other compounds. Some combustible gas and a solid residue of possible value for road use were also obtained.

INTRODUCTION

In the southern half of Iowa the Pennsylvania sediments are made up largely of clays and shales. Many of the shales are associated with coal seams and contain bituminous material. They may form an overburden on the coal seams of a few inches to as 35 feet or even more. The carbonaceous content of these shales varies considerably, as is obvious from the variation in color through shades of gray to black and from analytical data. The shales constitute a considerable part of the familiar "gob" piles at mine sites.

Because of the scarcity of good road building materials in southern Iowa there has been considerable interest in modifying these shales by heat treatment to use in place of limestone or gravel. As a result a research project sponsored by the Iowa State Highway Commission* has been carried out by the chemical engineering group in the Iowa Engineering Experiment Station at Iowa State University of Science and Technology, Ames, Iowa. Most of the work was concerned with burning the carbonaceous portion of the shale to produce heat enough to convert the inorganic portion of the shale into a product with sufficient strength and abrasion resistance to serve as road material. In addition work was carried out on the destructive distillation of the

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* Iowa Highway Research Board Project HR-32.

shale with the possibility of utilizing both the residual and the by products. Significant data from this work is summarized in this paper.

While extensive studies have been made on the destructive distillation of oil shale little apparently has been done on the shales of the Iowa coal field type. Barrett (1) reports that "dark brown or black carbonaceous or bituminous shales" are found "widespread and abundant" in the Pennsylvania system in Illinois. When destructively distilled some of these yielded from 11 to 15 gallons of "tar" per ton. About one half of this boiled below 95°C, about 40 percent between 95 and 125°C. About 3000 cubic feet of gas averaging 675 Btu was also produced. One sample yielded 6130 cubic feet of gas when heated 1080°C. The gas analyzed 35.4 of carbon dioxide and hydrogen sulfide, 43.6 percent carbon monoxide, and lesser amounts of hydrogen, nitrogen, and oxygen. In addition there was a small amount of a thin oil and a readily powdered gray black residue.

The shales in this study all came from the counties of Appanoose, Mahaska, and Marion in southern Iowa. They were present in strata varying from a few inches to 20 feet thick overlying the coal seams. They varied in calorific value from 230 to 6050 Btu, in volatile content from 7.7 to 36.4 percent, and in silica content from 2.30 to 59.8 per cent (2) Spectrographic analyses gave the following typical results: aluminum oxide, 10 per cent; calcium oxide, 15 percent; iron, between 5 and 10 percent; and traces of beryllium, copper, lithium, magnesium, nickel, strontium and titanium. Extraction of three typical shales in a soxhlet apparatus for two hours with commercial hexane and with benzol dissolved less than one percent. Trichloroethylene removed 1.23 percent from one sample. Methylene chloride and perchlorethylene removed less than one per cent in a four-hour period.

FISCHER RETORT WORK

Various samples of shales were assayed by the method developed by the U. S. Bureau of Mines for oil shale (4). Shale ground to 8-mesh was heated in a modified Fishcher retort at 500°C for one hour out of contact with air. The distillate was

Table 1. Results of Shale Assays Compared with Other Analytical Data

Sample No.	Oil Gal./ton	Calorific Value, Btu	Volatility Per cent	Silica Per cent
4	0.4	230	9.1	57.2
16	0.5	360		
12	0.7	600	10.2	47.9
2	0.8	1225	16.2	46.4
8	1.0	2075	21.9	40.4
10	23.2	6050	43.3	23.0

condensed at 0°C and centrifuged to separate the oil and water. Results calculated to gallons of oil per ton are shown in Table 1 with the corresponding calorific values, percent volatile, and percent silica. As might be expected the amount of oil increases with the increase in calorific value and volatile and with the decrease in silica.

GAS-FIRED RETORT STUDIES

Samples were destructively distilled by heating approximately 1000 grams to a maximum of from 721° to 1010°C in a gas-fired retort. In most cases the largest part of the distillate and gas came over below 540°C. The distillate, which was made up of a water and an oil layer, varied from 13.2 to 34.8 gallons per ton. From 520 to 4200 cubic feet of gas per ton varying from 270 to 480 btu per cubic foot were also produced. Distillation data for the oil produced in the Fischer retort assay and the oil produced in the gas-fired retort from the No. 10 sample are shown together for comparison in Table 2. The maximum temperature used to produce the gas-fired retort sample was 732°C. Curves plotted from these data are similar in shape each showing a definite break but with minor differences probably resulting from different heating rates and different maximum temperatures.

ELECTRICALLY HEATED RETORT STUDIES

The gas-fired retort was difficult to heat at a uniform and reproducible rate. A retort heated by a winding of electrical resistance wire was next employed (3). In the electrically heated retort samples were heated in the range 430° to 540°C for from 40 to 55 hours. The amounts of oil produced varied from 16.0 to 40.3 gallons per ton. Sample No. 10 produced 39.9 gallons per ton. No. 20 taken from the same mine as No. 10 but later produced 25.4 gallons per ton. No. 21 from the same general area, near Centerville, Iowa, produced 31.7 gallons. The composition of the No. 10 oil was determined by gas chromatography to be: pentene 1, 89.4 percent; and 2-methyl-butane 9.2 percent with small amounts of butyne, 1, 2-methyl-butanol-2, 1,3,4,5-tetramethyl benzene, 2,4,6-trimethyl phenol, and 2-methyl butanol-1. The major constituent of No. 20 was pentadiene-1,3. No. 21 produced mainly pentane and pentadiene-1,3. These compounds are lower boiling than most of those secured from the gas-fired retort. In the thermal break-down which occurs both the temperature and rate of heating affect the nature of the products.

Table 2. Distillation Results of Oil from Sample II-B-10

Temperature °C	Distillate in ml.	
	Fischer Retort	Gas Fired Retort
87.5	0.05	..
92.5	1.00	..

94.5	..	0.1
100.2	..	10.0
109.8	..	20.0
110.3	..	30.0
112.0	..	40.0
115.0	..	50.0*
123.5	2.00	..
128.5	2.50	..
135.0	3.00	..
136.2	4.00	..
225.5	..	50.1
269.4	..	51.9
272.8	..	52.0
279.1	..	52.5
280.3	..	53.0
281.4	..	53.5
283.1	..	54.0
284.7	..	54.5
295.8	..	55.0
296.3	..	55.5
302.4	..	56.0
304.5	..	56.5
306.7	..	57.0
308.9	..	57.5
312.2	..	58.0
315.0	..	58.5
316.7	..	59.0
316.9	4.05	..
320.0	..	59.5
320.6	..	60.0
327.8	4.38	60.5
328.9	..	61.0
333.3	4.60	61.5
335.0	..	62.0
336.0	5.00	..
337.8	..	62.5
340.0	5.50	63.0
342.2	..	63.5
343.9	..	64.0
346.1	6.00	64.5
346.7	..	65.0
347.8	..	65.5
348.9	..	66.0
349.4	..	66.5
350.0	..	67.0
350.0	..	67.5
350.0	..	68.0
358.0	6.05	68.5
360.0	6.50	..
393.9	7.50	..
396.6	8.00	..
404.5	8.50**	..

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

** Residue: Viscous heavy oil, solidified on standing.

THE SOLID RESIDUE

The solid residue after destructive distillation was tested for abrasion wear using a modification of the "Los Angeles" abrasion test (ASTM—C 131-46). Instead of the steel cylinder specified for this test a small ball mill was used, and the results were calculated to the equivalent standard value by a relationship developed by Frush (2). Abrasive wear on a series of eight samples varied from 37.0 to 80.0 per cent. No. 10 showed an abrasive wear of 48.0 percent. This had been heated to a maximum of 893°C. Frush has shown that abrasive wear decreases with temperature up to 1094°C. He also shows abrasive wear results on 14 naturally burned samples varying from 24.3 to 93.4 per cent.

DISCUSSION

Data have been presented in an effort to show the range of values of representative samples rather than to give all the data determined. The results using the Fischer retort technique are of possible interest in comparing with similar data in the technical literature on oil shale. Because of the better heat control which is possible the results secured with the electrically heated retort are of greater value than those secured with the gas-fired retort. Since the products of destructive distillation of the same shale will vary with temperature and time, any consideration of possible commercialization should be preceded by additional distillation. While it is known that large amounts of these shales exist in Iowa, detailed knowledge of available tonnage of the shales of different compositions is lacking. The analytical results identifying the products of distillation which were determined by gas chromatography should be spot-checked at least by independent methods. The products secured to date are probably not of sufficient value for commercial development.

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