

Steinschneider and his associates, Singer and Porges, has already been referred to.¹⁴ In this recent paper Steinschneider referred to plants operating in America, employing 5 to 25 mm. absolute pressure, but did not state what plants or particular processes he had in mind. In the published discussion of the paper Dvorkovitz stated that while partial vacuum had long been used at Baku the high vacuum referred to by Steinschneider had not been used; Jenkin also stated that, while operation at 20 to 45 mm. absolute pressure seemed possible, "none of the five or six benches of Bruenn-Koenigsfelder stills with which I am acquainted normally operate at anything like this vacuum. The usual pressure varies between say 75 mm. and 110 mm., and if for some special reason they manage to reach 50 mm. it is considered something of an achievement."

This important technical advance—i. e., large-scale oil distillation at absolute pressures of less than 5 mm.—has required the painstaking development of a new distillation technic. The process has definitely established itself in the petroleum industry and, although it seems that all important technical advances must suffer a certain amount of litigation, it appears to the writer from the publication, prior patent art, and other available information that the credit for this commercial development falls to John E. Schulze.

Acknowledgment

The writer wishes to express his indebtedness to Mr. Schulze for permission to publish much of the data in the present paper.

¹⁴ See also Porges, U. S. Patent 1,011,079 (1911); Steinschneider, U. S. Patent 981,953 (1911) and 1,162,729 (1915).

Table V—Comparative Tests of Typical Light, Medium, and Heavy Oils

	ORDINARY Paraffin base	DISTILLATION Naphthene base	By high- vacuum distillation, narrow cut
<i>Light Oils</i>			
Gravity, ° A. P. I.	30	21	21
Flash, ° F.	405	320	360
Flash range, ° F.	{ 290 550	{ 250 460	{ 340 380
Viscosity at 100° F., sec. Saybolt	190	200	200
Viscosity range, 100° F., sec. Saybolt	{ 60 600	{ 60 2000	{ 100 300
Color, N. P. A.	2 ¹ / ₂	2 ¹ / ₂	1 ¹ / ₂
Pour test, A. S. T. M., ° F.	30	Below zero	Below zero
Initial boiling point at 1.5 mm., ° F.	374	320	400
Per cent distilled up to 450° F., 1.5 mm.	10	60	98
<i>Medium Oils</i>			
Gravity, ° A. P. I.	29	20.5	20.5
Flash, ° F.	425	330	380
Flash range, ° F.	{ 300 550	{ 255 480	{ 370 430
Viscosity at 100° F., sec. Saybolt	260	300	300
Viscosity range at 100° F., sec. Saybolt	{ 70 1400	{ 60 2200	{ 200 450
Color, N. P. A.	3 ¹ / ₂	3	2
Pour test, A. S. T. M., ° F.	35	Below zero	Below zero
Initial boiling point at 1.5 mm., ° F.	410	350	435
Per cent distilled up to 475° F., 1.5 mm.	22	46	98
<i>Heavy Oils</i>			
Gravity, ° A. P. I.	28.5	19.5	19.5
Flash, ° F.	435	360	400
Flash range, ° F.	{ 305 500	{ 260 510	{ 385 430
Viscosity at 100° F., sec. Saybolt	365	500	500
Viscosity range, 100° F., sec. Saybolt	{ 75 1600	{ 70 2400	{ 400 700
Color, N. P. A.	5	3 ¹ / ₂	2 ¹ / ₂
Pour test, A. S. T. M., ° F.	35	Below zero	Below zero
Initial boiling point at 1.5 mm., ° F.	437	390	440
Per cent distilled up to 500° F., 1.5 mm.	35	56	98

Oil-Bearing Shales in North Carolina¹

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A survey of the Deep River Valley oil-bearing shales together with their retort assays, shale analyses, tonnage yields, and the analytical distillation data of the oils.

A PREVIOUS investigation of one of the shales in the Deep River Valley coal fields of North Carolina² disclosed the presence of a large deposit of an oil-bearing shale with a low shale oil and ammonium sulfate content. A systematic study of all the possible oil-bearing shales of this field was undertaken to ascertain whether more extensive and richer deposits were available.

Shales Investigated

The oil-bearing shales that were studied are found in the carboniferous formation, overlying and underlying the coal measures in the Deep River Valley coal field of Moore, Lee, and Chatham Counties in North Carolina. The particular samples investigated were taken from the holdings of the Erskine-Ramsay Coal Company at Cumnock, from as many different locations on the face of the mine and in the different formations as were thought necessary to include all of the shales of the field. Since the field shows little variation in thickness of the various strata of rock and coal, the accompanying log table from a diamond drill hole, located approximately one-half mile southwest of the Cumnock shaft on the banks of the Deep River, gives a representative analysis of the locations and thickness of the various formations in this field.

Table I—Record of Diamond Drill Hole

Formation No.	From		To		Materials
	Ft.	In.	Ft.	In.	
1			0	7	Sand
2			7	14	Clay
3			14	30	Sand
4			30	32	Red shale
5			32	40	Gray shale
6			40	60	Red shale
7			60	86	Gray shale
8			86	91	Black slate
9			91	96	Gray slate
10			96	173	Hard gray sandstone (dark)
11			173	178	Gray shale
12			178	186	Black slate
13			186	238	Gray slate
14			238	244	Black slate
15			244	268	Gray slate
16			268	275	Black shale
17			275	297	Gray shale
18			297	330	Black slate
19			330	355	Gray slate
20			355	387	Black shale (oil-bearing)
21			387	564	Black slate
22			564	564	4
23			564	602	4
24			602	604	3
25			604	604	5
26			604	608	3
27			608	609	9
28			609	611	7
29			611	612	6
30			612	613	6
31			613	615	Fire clay
32			615	627	Slate
33			627	643	Fire clay
34			643	645	Black band (oil-bearing)
35			645	647	Coal (fair)
36			647	649	Black band (oil-bearing)
37			649	650	Sandstone

¹ Received March 3, 1926.

² Vilbrandt, *J. Elisha Mitchell Sci. Soc.*, **41**, 108 (1925).

Formations 26, 27, and 28 mark the present mining operations for the recovery of coal from No. 26 formation. The narrowness of the seam of coal makes it necessary to work under low head-room. No. 28 is too poor a grade of coal to mine for steam coal and probably also for powdered fuel, but if formations 27, 28, and 29 could be utilized for some commercial product, the effective height of the chambers could be increased to 8 feet. Two layers of fire clay totaling 16 feet 6 inches lie below these workings and above the lower coal seam No. 35. The coal in formation 35 has been found to be a good coal, but the thinness of the vein (1 foot, 10 inches) would require the removal of formations 34 and 36 with it to give ample working room for the removal of the coal.

The shale formations that were investigated in this field were 16, 20, 23, a composite of 27 and 29, and a composite of 34 and 36. Inability to reach several of the other formations necessitated their omission from the study. All these deposits outcrop in different areas in the Deep River Valley, and operations could be made at these surface outcroppings. A sample of selected "balls" which weighed from 20 to 50 pounds and which was found in formation 20 was also investigated. These "balls" were very heavy, very shiny in appearance on the outside, but with a dull gray, stony interior.

Analytical Data

Extraction with absolute alcohol, carbon disulfide, and ether showed no measurable extractables from 100-gram samples of the shales. The shales were analyzed for moisture and ash by the methods applied to coals by Griffin.³ The difference between 100 and the sum of these two values was called fixed carbon and volatile matter. The method of retort assay used was that recommended by the United States Bureau of Mines.⁴ A retort charge of 453.6 grams was used, the method modified to include the following apparatus: Onto the exit tube from the graduated receiving flask was attached an acid absorption tower for the ammonia in the gases, the scrubbed gases then passing through a Sargent wet test gas meter, thence to a Junker gas calorimeter for determining the heating value of the gases evolved. The analytical data thus obtained are given in Table II.

Table II—Analyses and Yields of Deep River Oil Shales

Sample	Formation No.	Spent shale Grams	Shale oil Cc.	Ammonium sulfate Grams	ANALYSIS OF ORIGINAL SHALES			
					Gas Cu. ft.	Moisture Percent	volatile carbon Percent	Ash Percent
1	16	383	16.0	1.824	0.88	0.36	27.29	72.35
2	20	383	18.5	2.161	1.35	0.48	28.57	70.95
3	23	358	24.0	2.712	1.47	1.03	35.13	63.84
4	27 and 29	348	6.8	1.970	0.35	0.85	27.33	71.80
5	34 and 36	403	13.0	1.852	1.63	1.42	24.43	74.05
6	Balls from 20	423	6.1	0.423	0.68	3.05	16.78	80.17

The ammonia was dissolved both in the water layer in the receiving flask and in the ammonia scrubbing tower. The ammonium sulfate yields given in Table II are the sum of the amounts caught in both vessels. Volume measurements of gas were made directly on Sargent wet test meter.

The gases evolved at the beginning and at the end of the retort assays were either of too poor a quality to burn or were given off at such a slow rate that the flame could not be maintained in the burner of the calorimeter. Toward the end of the assay of each shale a very rapid evolution of a noncombustible gas occurred.

The oils separated out rather sharply, were very dark in

color, highly limpid, and possessed a decided "cracked" gasoline odor together with the shale oil aroma.

The retort assay results were recalculated on the tonnage (2000 pounds) basis in order better to present the value of the shales, especially for the oil and ammonium sulfate contents. These recalculated data, together with the formation, thickness of seams from which the samples were taken, the volume of the gas, and the heating value of the combustible gases evolved, are given in Table III.

Table III—Tonnage Yields of Deep River Oil Shales

Sample	Formation No.	Formation	Thick-ness of seam Feet	Spent shale Lb./ton	Shale oil Gal./ton	Ammonium sulfate Lb./ton	Gas ft./ton	B. t. u.
1	16	Black shale	7	1695	30.4	8.03	1760	151
2	20	Black shale	32	1695	35.1	9.47	1350	222
3	23	Black slate and shale	8	1580	45.6	12.37	2940	269
4	27 and 29	Black band	2.5	1624	12.7	10.80	734	...
5	34 and 36	Black band	4.2	1780	24.7	8.28	3260	301
6	From No. 20	Black balls	...	1880	11.4	1.86	1360	140

A comparison of the Deep River shales with those of other sections of the United States according to yields of ammonium sulfate and oil indicates that the shales of this North Carolina field are in general below those of the other fields of the United States in ammonium sulfate yield, but that they compare favorably in oil yield. The average yield of shale oil for the field would probably be around 30 gallons per ton.

Distillation Products from Shale Oil

The distillation products in these shales were determined as follows: The stoppered graduate containing the shale oil and water was allowed to stand overnight in a warm water bath. After reading the oil and water levels, the graduate and contents were cooled and weighed, and the contents were poured into a separatory funnel, together with 25 cc. of gasoline to facilitate the separation. The water was then drawn off and weighed, and from the weights and volume of oil obtained, the gravity of the oil was determined. The shale oil and gasoline were then run into an Engler distilling flask and fractionated, deducting 24 cc. from the first distillate as representing the gasoline distilled over at 150° C. on the basis of 96 per cent recovery of the gasoline added. Table IV gives the percentage yields of the various cracked products obtained from the oils.

Table IV—Analytical Distillation Data of Deep River Shale Oils

Sample	Formation No.	Specific gravity 20°/20° C.	FRACTIONS DISTILLING OVER				Still coke %	Loss %
			Below 150° C. %	to 250° C. %	to 350° C. %	Above 350° C. %		
1	16	0.789	13	20	39	20	4	
2	20	0.787	13	20	39	20	5	
3	23	0.811	15	21	40	12	4	
4	27 and 29	0.790	13	18	39	18	5	
5	34 and 36	0.790	10	25	27	10	9	
6	Balls	0.790	4	18	30	9	12	

It is apparent from the distillation data that the oils obtained are of somewhat the same composition, the first four samples yielding practically the same quantity of fractions. The lower boiling fractions approximate one-third of the oil; if that portion distilling over between 250° and 350° C. were to be re-cracked, the yield of motor spirits from these shales would run very high. Although the grade of lubricating oil obtained from shale will not at present stand up under heavy service conditions, research may show the way to treat or refine these oils to produce oils that will stand up as well as the petroleum lubricants.

Economic Status of the Deep River Field

The Deep River field has been estimated to contain from 70 to 100 million tons of coal in sight. On the basis of these estimates and the thickness of the different seams of shale

³ "Technical Methods of Analysis," 1st ed., 1921, p. 173. McGraw-Hill Book Co., New York.

⁴ Repts. of Investigations 2229 (1921).

and coal in this region, an approximation of one billion tons of oil bearing shale can be made. The utilization of all of this shale would yield on the basis of the retort assay results obtained in this investigation, a possible production of 27 billion gallons of shale oil and 47,500 tons of ammonium sulfate.

It can therefore be seen that these shales should be utilized. Probably all of this shale is not available for utilization owing to underground mining conditions, but about the same proportion of shale is available for utilization as that of the coal that can be mined from the field. At present the daily tonnage of coal taken from the field is about 400 tons, but this will shortly be increased by the introduction of newer and more modern transportation equipment. With the utiliza-

tion of some of the shales, making working conditions better in the mines, tonnage of coal and shale can be jointly increased.

The actual cost of the production of a barrel of shale oil in this field cannot be estimated, but when one considers what difficulties must be met before the shales in the Rocky Mountains become available, outcropping up in the walls of the canyons and lying at altitudes of 4500 and 8000 feet, one can understand that the difficulties in mining in the Deep River field are not insurmountable. Many mining engineers claim that the western shales will cost about as much for mining as coal, since coal mining conditions will have to be met. The same cost figures as apply to the coal mining operations in this field should then apply to the mining of shale.

Specific Heats of Oils¹

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THE importance of specific heat data for oils in problems of the design and testing of plant equipment justifies a more extensive investigation of the subject, particularly at high temperatures, than has yet been reported. This paper presents (1) the results of experiments on the specific heats of a number of oils encountered in the refinery, (2) a general equation involving temperature and specific gravity which correlates these data for engineering purposes, and (3) a comparison between the equation and other results reported in the literature.

Experimental Method

The experimental method consisted of measuring the temperature rise when a definite amount of electrical energy was put into the oil, and is similar to that described by Bailey and Edwards.² From the recorded electrical input two corrections were subtracted before calculating the specific heat of the oil—the water equivalent of the calorimeter at the average temperature of the experiment, and a radiation correction. The latter was estimated by allowing the oil to cool from the higher to the lower temperature and calculating the cooling rate due to radiation. A line drawing of the apparatus to scale is shown in Figure 1.

The container was a quart-size "Icy-Hot" thermos bottle in which a heating coil, a stirrer, and the sample of oil (530 to 680 grams) were placed and heated to a steady initial temperature. The current was supplied by a 24-volt storage battery, and a wattmeter (Weston Model 310 Portable) was used to measure the energy input. This was a new

The specific heats of fifteen petroleum oils have been determined over temperature intervals varying from 50° to 430° F. The results may be expressed by the equation

$$C = \frac{(t + 670)(2.10 - \text{sp. gr.})}{2030}$$

where C = the specific heat

t = the temperature in ° F.

and sp. gr. = the specific gravity of the oil at 60° F.

The equation fits the data with an average deviation of 2.3 per cent at 240° F. and represents oils whose specific gravity at 60° F. varied from 0.75 to 1.00.

This equation, representing the variation of specific heat with temperature and with specific gravity, agrees reasonably well with the average of other specific heat data available in the literature both at 60° F. and at higher temperatures.

wattmeter with a guaranteed accuracy of 0.25 per cent of full-scale deflection (125 watts), and a factor of 0.9964 was used to correct for energy used by the meter. Allowance was made for errors due to residual magnetism in the coils by reversing the current during the check determination of specific heat and using the average of the two current readings. The stirrer was regulated to a speed of about 500 r. p. m. Three thermometers, certified by the Bureau of Standards, were employed in measuring oil temperatures. They covered the following ranges:

0° to 112° C. at 0.1° intervals, 86° emergent
90° to 202° C. at 0.1° intervals, 78° emergent
200° to 300° C. at 0.2° intervals, 80° emergent

The observations upon the oils during the first part of the work were made with the thermos bottle unprotected except for the jacket supplied by the makers. It was found that at the higher temperatures the radiation correction became so large in comparison to the temperature rise that the accuracy was limited. The jacket was then lagged with felt (Nos. 8, 10, and 11), but even this change did not eliminate the difficulty. Therefore, in later work (Nos. 2, 3, and 12 to 18, inclusive) the whole apparatus was surrounded by an air jacket which was maintained at the mean temperature of the particular interval over which the observations were taken. This interval was from 15° to 25° C., read to the nearest 0.03 degree. Thus the radiation was taking place between two surfaces which had never more than 12.5 degrees difference in temperature and the difference during the first half of the run was equal to that during the second half of the run but opposite in sign.

In order to secure an even temperature in the air jacket a fan was installed in the bottom. Exploration of the chamber showed that the temperature was fairly uniform through-

¹ Presented under the title "The Specific Heats of Petroleum Oils" before the Division of Petroleum Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

² THIS JOURNAL, 12, 891 (1920).