Survey of Qusseir Shales and other Carbonaceous Shales in Egypt

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Fifty one samples of carbonaceous shales were collected from different localities of Egypt, U. A. R. and subjected for general analysis. Three samples of these from the area between Gebel Hamadat and Gebel Dawi (Qusseir) were chosen for detailed analysis.

MINERALOGICAL examination of Qusseir carbonaceous shales showed that it consists predominantly of banded clay with dissemenated carbonaceous matter and shells of foraminefera. The carbon, hydrogen, nitrogen, ash contents, and gross calorific values are similiar to those of Volga inflammable shales mined in U. S. S. R.

The ash is rich in calcium oxide content and could be employed in civil engineering. The Qusseir carbonaceous shales are a very low grade fuel and have high sulfur and volatile sulfur contents. The amount of organic matter, 22% kerogen in Qusseir's carbonaceous shale, is comparable to the shales mined in Colorado, U. S. A. The C:H ratio of Qusseir's oil shale is not as high (*9*) considering that organic material with highest C:H ratio yielded the least oil. Shale oil contains 44% petroleum fraction and 3% light fraction which indicates a deficiency in low boiling material. The C:H ratio of Qusseir's shale oil is 8.45 indicating high degree of aromaticity. The carbonizing gas represents a good quality of gaseous fuel (30–34 H_2 and 4046–4235 kcal./Nm^3).

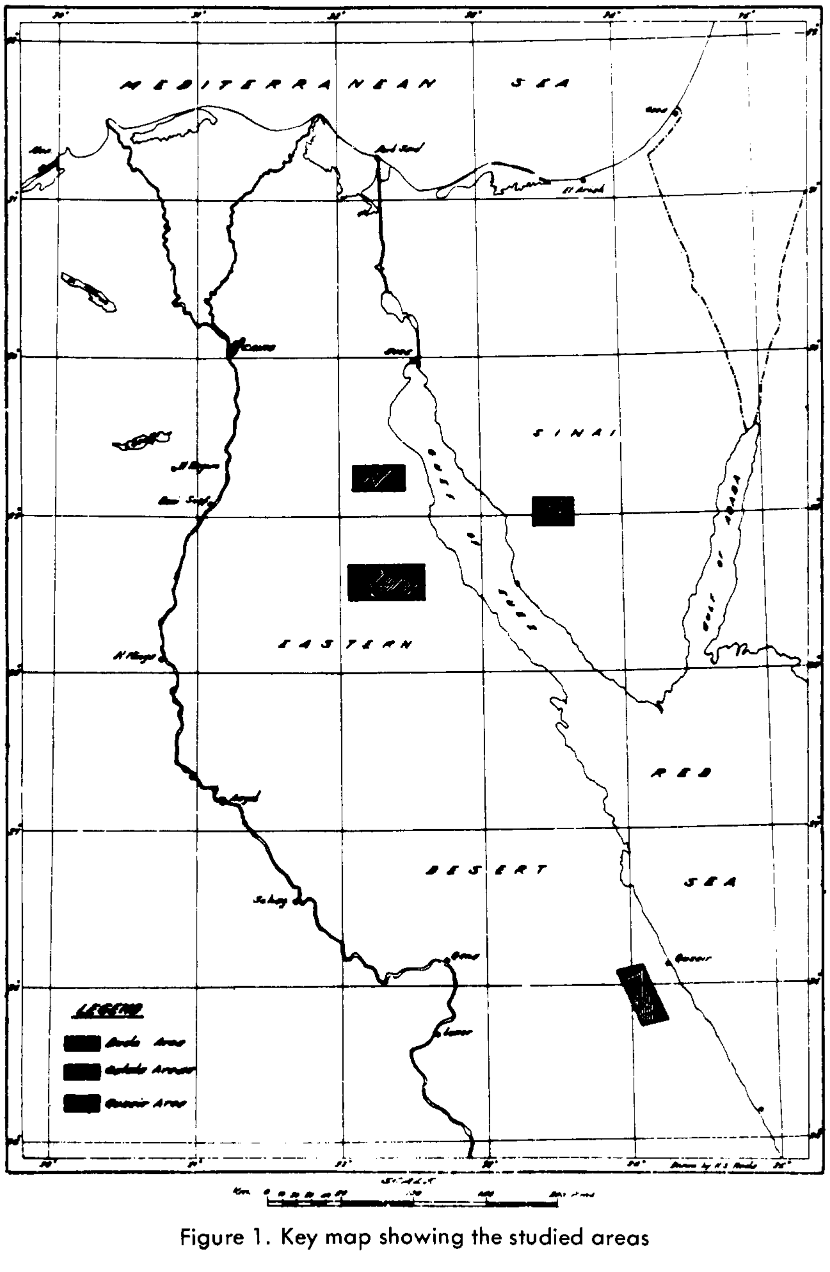

Figure 1. Key map showing the studied areas

GEOLOGICAL DESCRIPTION FOR THE CARBONACEOUS SHALE

Fifty one samples, representing the carbonaceous shale beds in Egypt (Figure 1), were collected and subjected to general discussion and preliminary analysis.

Sixteen samples were collected from Galalah Area, 10 samples represent Galalah Kebleih (Umm Ortah Valley) (Figures 2, 3), and six samples from six different locations in Galalah Bahariya, G1–G16 (Figure 4). Eleven samples of carbonaceous material were analyzed from two wells in Buda Valley, Sinai (Figures 5, 6) (B1–B11). Twenty-four samples of carbonaceous shale from different phosphate mines at Qusseir Area were obtained for general study and chemical analysis (Q1–Q24). Three samples of these Q15, Q16, and Q17 from Abutundoub Bahariya, Dawi and Nakhel mines, representing the carbonaceous bed present in the area between mountain Hamadat to mountain Dawi (Figures 7, 8) were completely investigated. The carbonaceous materials range from 80–150 cm. in thickness. Located above them are sandy formations and below them are phosphate deposits of upper cretaceous age, a dominating formation in the area.

GENERAL ANALYSIS OF CARBONACEOUS SHALES

The samples were prepared (*3*) and analyzed for moisture, ash (*4*), total sulfur (*5*), and carbon dioxide (*21*). Also extraction of oil with benzol (*24*) was carried out. Results of analyses are recorded in Tables I and II.

The samples with the geological No. Q15, Q16, and Q17 were chosen for the present investigation because of their relatively high percentage of carbon content and they are present over a wide area of Upper Egypt, Qusseir (Figure 8).

DETAILED ANALYSES

Detailed analyses (*18, 20*) for these samples were carried out by the author in the Central Research Institute of Fuels in Prague, Czechoslovakia (Ustav Provyzkum a Vyuziti Paliv).

The samples were prepared (*9*) and analyzed for moisture, ash (*10*), and carbon dioxide (*14*) according to the Czechoslovakian standards. Crude oil was extracted with benzol from carbonaceous shale using infra red heating. Slightly higher results (0.1–0.3) were obtained than previously according to IP 53/55 (*24*).

Carbon dioxide was determined volumetrically by treating the ore with sulfuric acid and reacting the evolved carbon dioxide with excess sodium hydroxide.

The results of analyses for these experiments and for the following are arranged in Tables III and IV.

Phase Analyses of Sulfur (22). From the determination of total sulfur in coal (*10*) and total sulfur in ash (fixed sulfur), the value of volatile sulfur was calculated.

Acid soluble sulfates were determined by digesting coal with hydrochloric acid, and the sulfate ion in the filtrate was precipitated as barium sulfate. The residue of carbonaceous shale remaining after digestion with hydrochloric acid was treated with nitric acid and bromine water. The iron in the

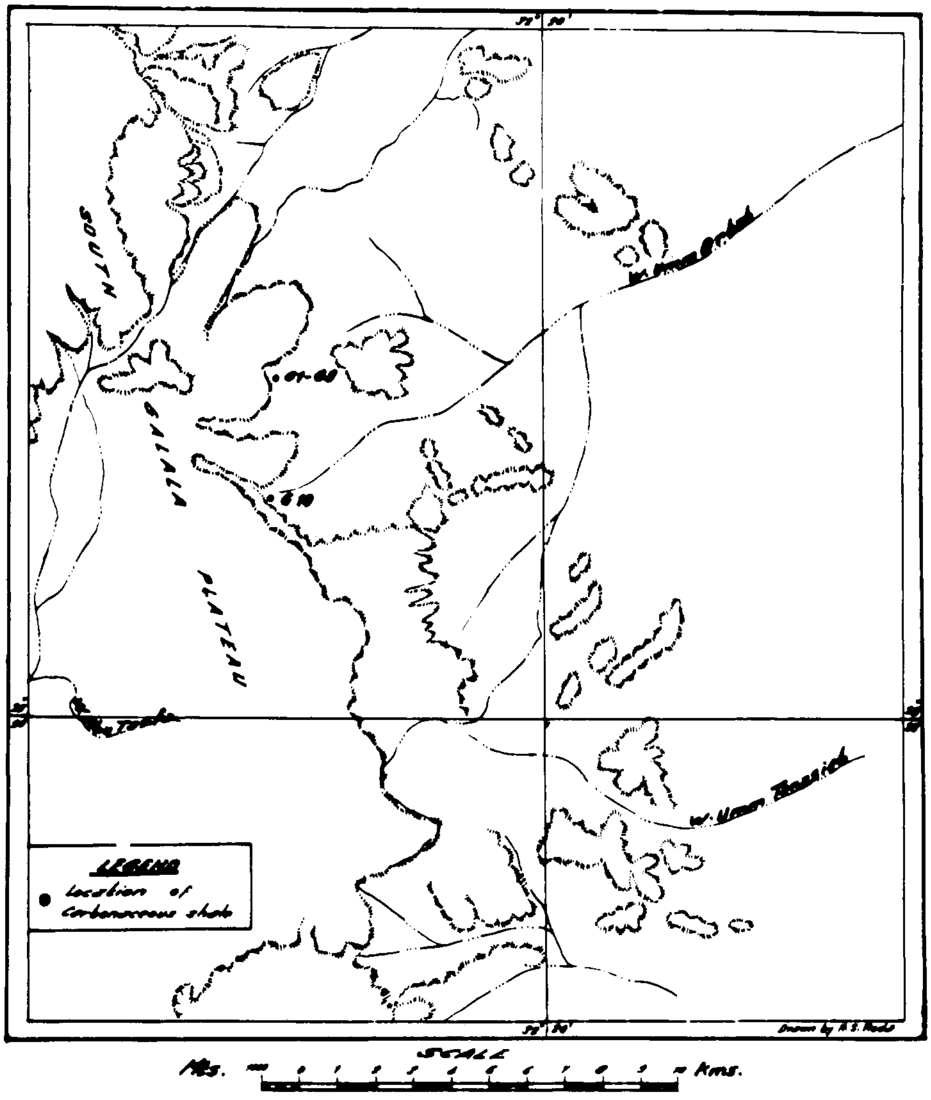

Figure 2. Location map of carbonaceous shale in Wadi Umm Ortah

Table I. Results of Analyses of Carbonaceous Shales for Moisture, Ash and Loss on Ignition °C.

Geological No.	Moisture %	Ash Anal. S.[a] %	L.O.I. Anal. S.[b]	Ash Dry S.[c]	L.O.I. Dry S.[d]
G1	4.70	82.20	13.10	86.25	13.75
G2	4.60	83.70	11.70	87.73	12.27
G3	0.40	86.50	13.10	86.84	13.16
G4	0.50	85.30	14.20	85.72	14.28
G5	0.98	83.90	15.20	84.66	15.34
G6	1.06	81.50	17.50	82.32	17.68
G7	1.51	78.40	20.10	79.59	20.41
G8	1.30	82.70	17.30	83.78	16.22
G9	0.60	79.20	20.20	79.67	20.33
G10	1.80	83.00	15.20	84.52	15.48
G11	1.70	69.50	28.80	70.70	29.30
G12	1.10	80.50	18.40	81.39	18.61
G13	6.10	47.90	46.00	51.01	48.99
G14	1.50	86.80	11.70	88.12	11.88
G15	1.70	80.30	18.00	81.68	18.32
G16	6.90	78.60	14.50	84.42	15.58
B1	1.51	83.44	15.05	84.69	15.31
B2	2.53	79.79	17.79	81.87	18.13
B3	2.65	79.89	17.46	82.07	17.93
B4	2.61	80.61	16.78	82.78	17.22
B5	2.37	80.67	16.96	82.63	17.37
B6	1.36	89.03	9.61	90.26	9.74
B7	1.90	73.72	24.33	75.20	24.80
B8	1.91	88.19	9.90	89.91	10.99
B9	1.79	90.20	8.01	91.85	8.15
B10	1.63	87.31	11.06	88.76	11.24
B11	0.78	74.97	24.25	75.56	24.44
Q1	2.56	78.50	18.94	80.56	19.44
Q2	5.53	76.60	17.87	81.08	18.92
Q3	9.18	82.90	7.92	91.27	8.73
Q4	11.72	81.86	6.42	92.72	7.28
Q5	9.91	81.09	9.00	90.00	10.00
Q6	10.46	74.53	15.01	83.23	16.77
Q7	9.80	79.12	11.08	87.71	12.29
Q8	9.04	79.66	11.30	87.57	12.43
Q9	10.66	79.58	9.76	89.07	10.93
Q10	10.28	82.32	7.4	90.74	9.26
Q11	3.98	90.60	5.42	51.35	48.65
Q12	9.50	77.90	12.60	85.18	14.82
Q13	2.04	88.86	9.06	90.71	9.29
Q14	2.26	89.52	8.24	91.58	8.42
Q15	2.90	66.00	31.10	67.97	32.03
Q16	3.49	67.05	29.46	69.47	30.53
Q17	2.99	68.62	28.39	70.73	29.27
Q18	2.48	76.60	20.92	78.54	21.46
Q19	3.34	80.46	16.20	83.24	16.76
Q20	1.42	79.89	18.69	81.69	18.96
Q21	2.54	75.90	21.56	77.87	22.13
Q22	2.72	79.50	17.78	81.72	18.28
Q23	3.38	81.30	15.32	84.14	15.86
Q24	6.07	78.40	15.53	83.03	16.97

[a] Anal. S. = Analytical sample. [b] L.O.I. = Loss on ignition. [c] Ash, dry sample = The ash is calculated to the dry base. [d] L.O.I., dry sample = The loss on ignition is calculated to dry base.

filtrate equivalent to pyritic sulfur was determined volumetrically.

Sulfide sulfur was estimated by treating coal with hydrochloric acid and absorption of hydrogen sulfide formed by cadmium acetate solution.

Organic sulfur = Total sulfur − sulfur of (acid soluble sulfates + pyritic sulfur + sulfides).

Determination of Total Carbon, Hydrogen & Nitrogen. Calculation of percentage of oxygen. Total carbon and hydrogen was determined by burning a weighed quantity of sample in a closed system, and fixing the products of combustion in an absorption train after complete oxidation and purification of interfering substances.

Organic carbon = total carbon − carbon corresponding to CO_2. The nitrogen (*13*) is converted into ammonium salts by destructive digestion and these salts were subsequently decomposed by hot alkaline solution from which the ammonia is recovered by distillation and finally determined by titration.

Oxygen % = 100 − (H + organic C + N + organic S) Moisture and Ash Free Sample.

Table II. Results of Analyses of Carbonaceous Shales for Total Sulfur, Extracted Oil and Carbon Dioxide

	Sample as Received			Dry Base		
Geological No.	Sulfur	Extracted oil	Carbon dioxide	Sulfur	Extracted oil	Carbon dioxide
Q 1	2.07	0.14	4.1	2.12	0.14	4.21
Q 2	2.55	0.05	3.5	2.70	0.05	3.71
Q 3	0.51	0.03	0.5	0.57	0.03	0.56
Q 4	2.36	0.03	0.5	2.67	0.03	0.57
Q 5	4.11	0.10	2.1	4.56	0.11	2.33
Q 6	2.59	0.08	3.9	2.89	0.09	4.36
Q 7	2.33	0.09	1.5	2.58	0.10	1.66
Q 8	4.53	0.02	1.7	4.98	0.02	1.87
Q 9	1.03	0.03	3.3	1.15	0.03	3.69
Q 10	1.68	0.04	1.7	1.87	0.04	1.89
Q 11	1.15	0.03	2.5	1.20	0.03	2.60
Q 12		0.09	2.2		0.10	2.43
Q 13		0.05	6.4		0.05	6.53
Q 14		0.07	6.8		0.07	6.55
Q 15		1.20	11.00		1.24	11.33
Q 16		1.00	10.60		1.04	10.98
Q 17	3.57	0.93	10.70	3.67	0.96	11.03
Q 18		0.06	8.00		0.06	8.20
Q 19		0.35	4.0		0.36	4.14
Q 20		0.20	4.0		0.20	4.06
Q 21		0.34	3.0		0.35	3.07
Q 22		0.26	5.2		0.27	5.35
Q 23		0.30	3.52		0.31	3.64
Q 24		0.06	4.18		0.06	4.45

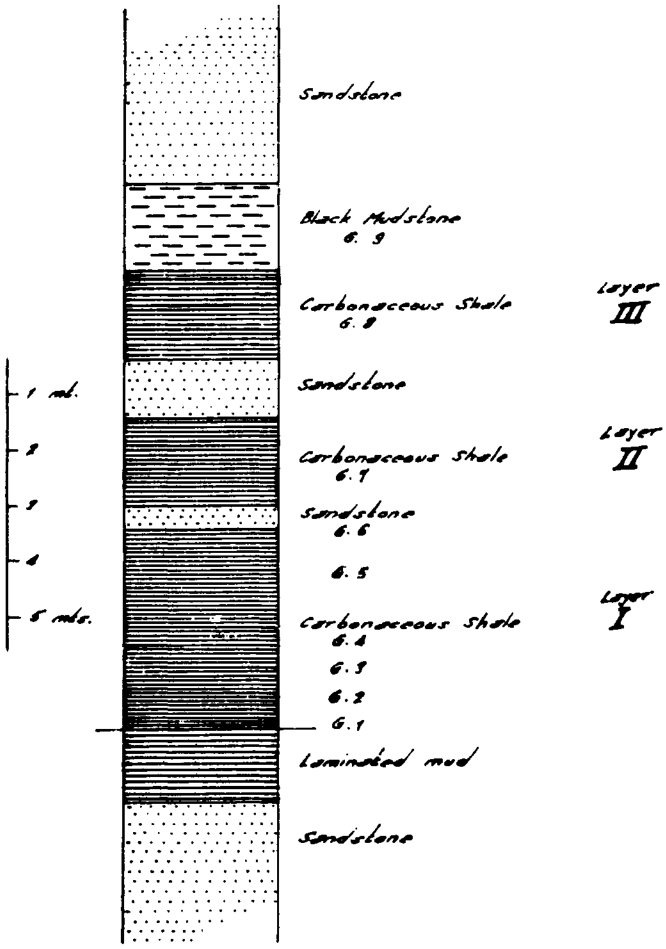

Figure 3. Profile section showing the carbonaceous layers at Umm Ortah

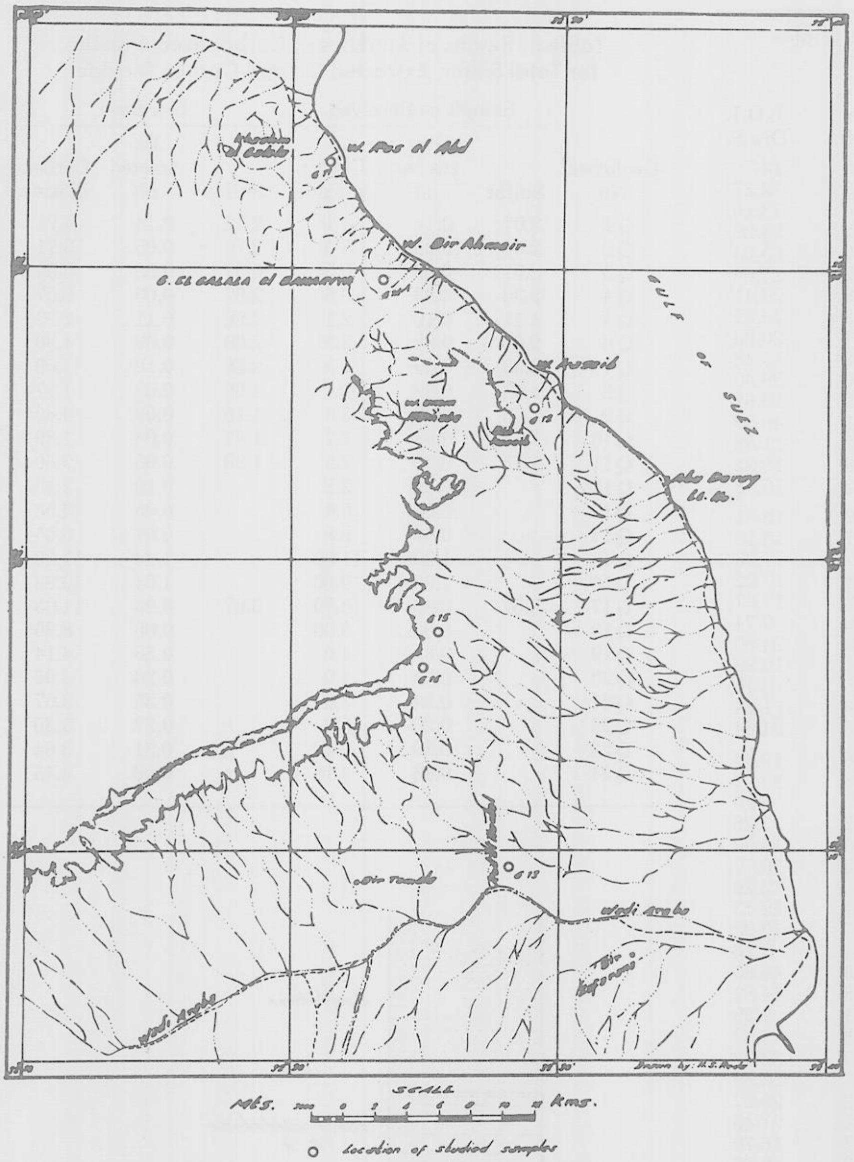

Figure 4. Location map of El Galala El Baharia

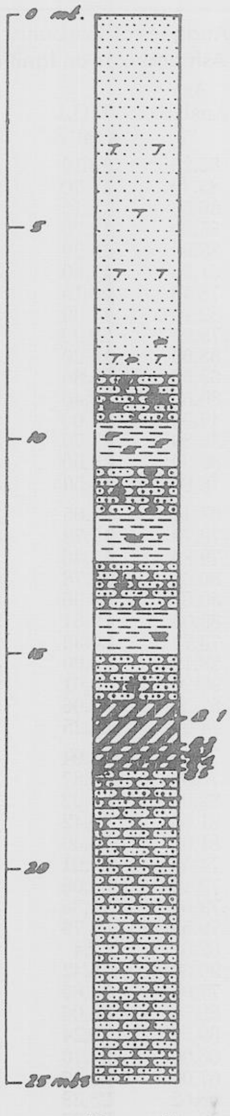

Figure 5. Buda Well, No. 1, scale 1:100

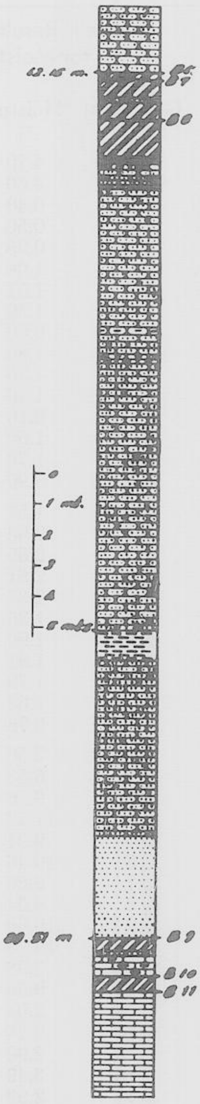

Figure 6. Buda Well, No. 2, scale 1:100

Determination of Volatile Matter. Calculation of fixed carbon. The volatile matter was determined according to the Czechoslovakian standard (*11*) and corrected according to the following:

Volatile matter (actually present) % = loss of weight according to the standard − water W % − carbon dioxide % − 0.09 ash − 0.4344 pyritic sulfur.

The mineral content is calculated from the following formula: Mineral content % = 1.1 ash estimated + 0.4344 pyritic S + 0.82 carbon dioxide + 2.75 (sulfate sulfur in shale − sulfur in ash).

The hydrogen content is corrected for mineral hydrogen derived from lattice water of clays. H = H analyzed sample − 0.01 ash + 0.01 pyritic sulfur + 0.01 CO_2.

Organic matter % = 100 − mineral content − W content.

Therefore, the fixed carbon "involatile matter" % = real content of organic matter − volatile matter.

Gross and Net Calorific Values. The gross calorific value was experimentally determined (*12*) by burning a known weight of carbonaceous shale (oxygen atmosphere) in a calorimetric bomb at constant volume and recording the total increase of temperature.

The net calorific value was calculated by subtracting the heat of vaporization of the water content in the fuel, and that of water formed by burning the hydrogen content of the carbonaceous shale from the gross calorific value.

Spectrographic Examination of the Ash. A Hilger large quartz spectrograph was used for semiquantitative analyses of the ash of carbonaceous shale Q15, Q16, and Q17. The sample was placed in a hole 10 mm. deep and 1.2 mm. diameter, in spectrographically pure carbon electrodes, anode exitation.

The arc was maintained using 220 volt and 8 amperes A.C. The time of exposure was 60 seconds for ultraviolet region and 15 seconds for the visible region. The range was 240–3500 A. and 3000–6000 A.

The plates used were KSAI, superorthochromatic 9 × 24 cms. The developer was blue rapid type of Agfa spectral plate.

The concentration of the elements was determined from the relative intensities of the spectral lines. The limit of sensitivity of detection differs with different elements but the method used could detect generally up to 0.001%.

Results of analyses are given in Table V.

Analysis of Ash. The sample for analysis was prepared and analyzed according to the Czechoslovakian Standards (*10, 15*). Silica was determined gravimetrically by volatilization as SiF_4. Iron was determined volumetrically, dichromate method. Aluminium was determined gravimetrically as aluminium oxinate. Calcium was determined volumetrically by titrating calcium oxalate with potassium permanganate. Magnesium and phosphorous were deter-

Table III. Classical Analyses of Qusseir Samples No. Q15, Q16, and Q17

	Q15				Q16				Q17			
Sample No.	Lab. S.[a]	Anal. S.[b]	Dry S.	M.A.F.S.[c]	Lab. S.	Anal. S.	Dry S.	M.A.F.S.	Lab. S.	Anal. S.	Dry S.	M.A.F.S
Moisture %	3.12	3.06			3.17	2.57			3.12	2.71		
Ash %	62.68	62.72	64.70		63.52	63.92	65.60		62.68	62.95	64.70	
Loss on ignition %	34.20	34.22	35.30	100.00	33.31	33.51	34.40	100.00	34.20	34.34	35.30	100.00
Gross calorific value, kcal./kg.	1914	1915	1976	5596	1922	1934	1985	5771	1928	1936	1990	5638
Net calorific value, kcal./kg.	1784	1785	1859	5268	1799	1794	1857	5399	1781	1790	1857	5260
Hydrogen %	2.12	2.12	2.19	6.20	2.37	2.38	2.44	7.10	2.47	2.48	2.55	7.22
Total carbon %	20.37	20.38	21.02	59.56	19.10	19.22	19.73	57.35	20.38	20.47	21.04	59.61
Organic sulfur %	1.62	1.62	1.68	4.73	1.73	1.74	1.79	5.19	1.74	1.74	1.83	5.07
Nitrogen %	0.48	0.48	0.49	1.40	0.49	0.49	0.50	1.46	0.33	0.33	0.34	0.96
Oxygen %	9.61	9.62	9.92	28.11	9.62	9.68	9.94	28.90	9.28	9.32	9.58	27.14
Total sulfur %	3.60	3.60	3.71		3.79	3.81	3.91		3.35	3.36	3.45	
Sulfur of sulfates %	0.13	0.13	0.13		0.12	0.12	0.12		0.15	0.15	0.15	
Sulfur of pyrites %	1.82	1.82	1.87		1.89	1.90	1.95		1.41	1.42	1.42	
Sulfur of sulfides %	0.032	0.032	0.033		0.048	0.048	0.049		0.049	0.049	0.050	
Carbon dioxide %	13.24	13.25	13.67		12.67	12.75	13.07		11.58	11.63	11.95	

[a] Lab. S. = Laboratory sample (as received). [b] Anal. S. = Analytical sample, (Air dried). [c] M.A.F.S. = Moisture and Ash Free sample.

Table IV. Results of Analyses are Calculated with Respect to Mineral Matter and Total Organic Matter

	Q15				Q16				Q17			
Sample No.	Lab. S.[a]	Anal. S.[b]	Dry S.	D.M.F.S.[c]	Lab. S.	Anal. S.	Dry S.	D.M.F.S.	Lab. S.	Anal. S.	Dry S.	D.M.F.S.
Moisture %	3.12	3.06			3.17	2.57			3.12	2.71		
Mineral matter %	75.81	75.86	78.25		75.21	75.68	77.68		74.76	75.08	77.17	
Organic matter %	21.07	21.08	21.75	100.00	21.61	21.75	22.32	100.00	22.12	22.21	22.83	100.00
Gross calorific value kcal./kg.	1914	1915	1976	9084	1922	1934	1985	8892	1928	1936	1990	8717
Net calorific value kcal./kg.	1784	1785	1859	8552	1779	1794	1857	8319	1781	1790	1856	8132
Volatile matter %	7.64	7.65	7.89	36.29	10.17	10.23	10.50	47.03	12.30	12.58	12.93	56.64
Fixed carbon %	13.42	13.43	13.85	63.71	11.45	11.52	11.82	52.97	9.59	9.63	9.90	43.36
Hydrogen %	1.64	1.64	1.69	7.78	1.88	1.89	1.94	8.69	1.98	1.98	2.04	8.92
Organic carbon %	16.67	16.77	17.30	79.54	15.64	15.74	16.16	72.37	17.27	17.30	17.78	77.89
Organic sulfur %	1.62	1.62	1.68	7.69	1.73	1.74	1.79	8.00	1.74	1.74	1.83	7.83
Nitrogen %	0.48	0.48	0.49	2.28	0.49	0.49	0.50	2.25	0.33	0.33	0.34	1.49
Oxygen %	0.57	0.57	0.59	2.71	1.88	1.89	1.94	8.69	0.86	0.86	0.88	3.87
Total sulfur %	3.60	3.60	3.70		3.79	3.81	3.91		3.35	3.36	3.45	
Sulfur of sulfates %	0.13	0.13	0.13		0.12	0.12	0.12		0.15	0.15	0.15	
Sulfur of pyrites %	1.82	1.82	1.82		1.89	1.90	1.95		1.41	1.42	1.42	
Sulfur of sulfides %	0.032	0.032	0.032		0.048	0.048	0.049		0.049	0.049	0.050	

[a] Lab. S. = Laboratory sample (as received). [b] Anal. S. = Analytical sample (Air dried). [c] D.M.F.S. = Dry Mineral matter free sample.

mined gravimetrically as magnesium pyrophosphate. Sulfur was determined gravimetrically as barium sulfate. Titanium was determined colorimetrically using hydrogen peroxide. Results of analyses are recorded in Table VI.

TESTS CONCERNING QUANTITY AND QUALITY OF OILS AND GASES

Xylene Distillation. Twenty grams of the laboratory samples were distilled with xylene moisture free and the distillate was collected in a saturated xylene solution.

Carbonization at Low Temperature. The apparatus (Figure 9) and procedure used was according to the Czechoslovakian Standards (*16*). The maximum temperature recorded during carbonization was 550° C. Since products of distillation might be destructed by prolonged heating or abrupt rising of temperature, the rise of temperature with respect to time was maintained as follows.

Rise of Temperature with respect to Time

Minutes	Temp. ° C.	Minutes	Temp. ° C.
10	100	60	375
15	140	65	400
20	165	70	425
25	195	75	450
30	220	80	475
35	240	85	490
40	275	90	510
45	300	95	520
50	325	100	520
55	350	105	520

The total time of the procedure was 105 minutes. The compounds that were evolved during the test were condensed in the flask and gases were collected. The collecting liquid of the gas was a saturated solution of sodium chloride in distilled water and the solution was acidified using methyl orange as indicator.

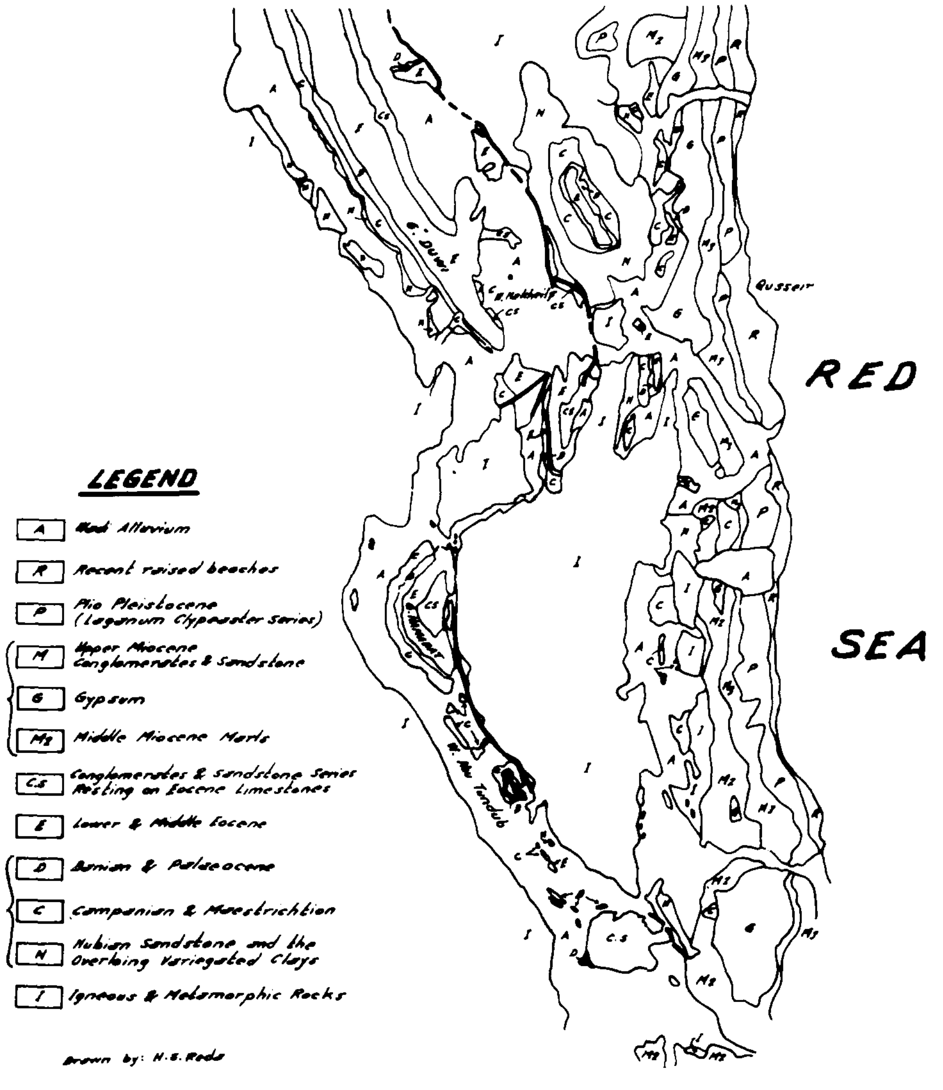

Figure 7. Geological map of Qusseir area (after M.I. Youssef)

Table V. Spectrographic Examination of Qusseir's Shale Ash Semiquantitative Analysis

Sample No.	Above 1%	Between 1% and 0.1	Between 0.1 and 0.01	Below 0.01
Q15	Si, Ca, Al, Fe, P, K, Na, Mg	Zn, Ti, Mn	Cr, Cu, Ag, Mo, Cd, V, Ni	B, Ga, Pb, Ba, Sn, Yb
Q16	Si, Ca, Al, P, Fe, K, Mg, Na	Zn, Ti, Mn	Cr, Cu, Mo, V	Ag, B, Ga, Pb, Ba, Sn, Yb, Ni, Cd,
Q17	P, Fe, Na, Si, Ca, Al, Mg, K	Zn, Ti, Mn	Cr, Cu, Mo, V, Cd, Ni	Ag, B, Ga, Ba, Pb, Sn, Yb

The elements which are not detected: As, Be, Bi, Ce, Co, Ge, In, La, Li, Nb, Sb, Sc, Ta, Th, Te, W, Y, Zr.

The retort containing semicoke was weighed and per cent semicoke was obtained. The water in the collecting flask was determined using xylene distillation.

The water of carbonization can be estimated by subtracting the moisture of the analytical sample from total water.

The flask containing the oil was swept, dried, and weighed and the per cent of oil was determined.

The volume of gas and conditions under which the gas was collected (pressure and temperature) were recorded and the corrected volume for gas obtained by carbonization of one kg. of carbonaceous shale was obtained.

Results of analyses are recorded in Table VII.

Some Specifications of the Oil Produced by Distillation. Determination of specific gravity (*1*), elementary analysis of oil (C and H), and fractional distillation (*2*) of the oil were obtained by carbonization of Qusseir's carbonaceous shale. The heat used for fractional distillation of the oil was regulated in such a way that the distillation proceeded at 8 ml./min. The fractions were separated at these temperatures: 110°, 160°, 190°, 220°, 250°, 280°, 310°, and 350° C.

Results of analyses are recorded in Table VIII and the distillation curve is plotted in Figure 10.

Analysis of Gas. The volumetric chemical method for analysis of gas (*6*) was carried out on three gases obtained from carbonization of Qusseir's carbonaceous shales Q15, Q16, and Q17. The method combines absorption and combustion methods. Acids, gases, and unsaturated hydrocarbons were absorbed. Saturated hydrocarbons were burned with excess oxygen over hot platinum and the contraction, carbon dioxide produced, and oxygen con-

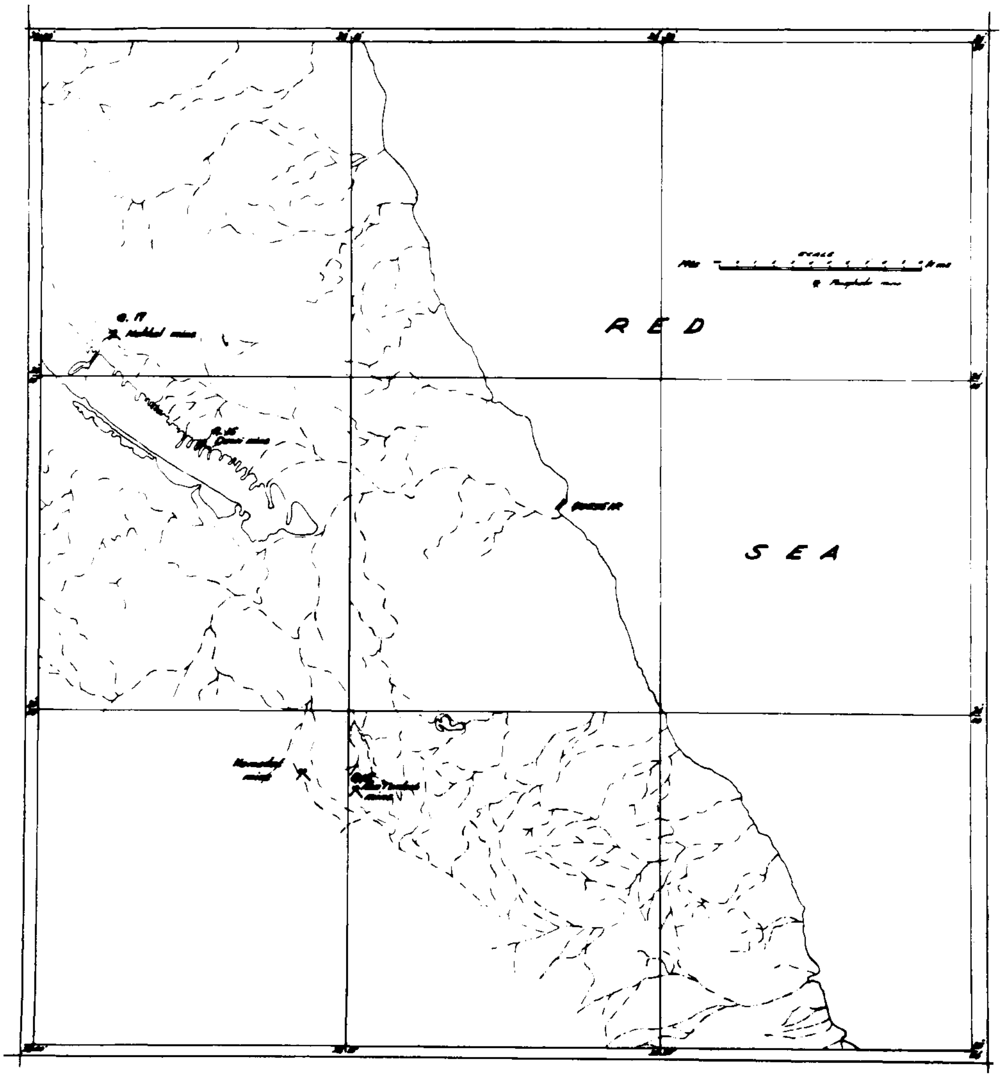

Figure 8. Location map of carbonaceous shale in Qusseir

Table VI. Analysis of Ash

	Q15		Q16		Q17	
	Ash	Anal. S.	Ash	Anal. S.	Ash	Anal. S.
Silicon dioxide SiO_2, %	37.21	23.34	34.47	22.03	35.87	22.58
Aluminium oxide Al_2O_3, %	11.12	6.97	10.28	6.57	10.26	6.46
Ferric oxide Fe_2O_3, %	5.37	3.37	7.62	4.87	4.25	2.68
Titanium dioxide TiO_2, %	0.50	0.31	0.50	0.31	0.55	0.34
Phosphorous pentoxide P_2O_5, %	3.53	2.21	3.77	2.41	4.86	3.06
Calcium oxide CaO, %	26.52	16.63	27.90	17.83	27.36	17.22
Magnesium oxide MgO, %	1.58	0.99	2.06	1.32	1.54	0.97
Sulfur trioxide SO_3, %	7.46	4.67	8.86	5.66	6.85	4.31

Table VII. Carbonization at Low Temperature

	Lab. S.^{a}	Anal. S.^{b}	Dry S.	M.A.F.S.^{c}
			Q15	
Moisture %	3.12	3.06	...	...
Ash %	62.68	62.72	64.70	...
Loss on ignition %	34.20	34.22	35.30	100.00
Water of carbonization %	2.94	2.94	3.03	8.59
Oil %	10.53	10.54	10.87	30.80
Semicoke %	77.81	77.86	80.32	44.24
Gas and losses %	5.60	5.60	5.78	16.37
			Q16	
Moisture %	3.17	2.57	...	...
Ash %	63.52	63.92	65.60	...
Loss on ignition %	33.30	33.51	34.40	100.00
Water of carbonization %	2.81	2.83	2.90	8.45
Oil %	10.51	10.58	10.86	31.57
Semicoke %	78.78	79.26	81.35	45.78
Gas and losses %	4.73	4.76	4.89	14.20
			Q17	
Moisture %	3.12	2.71	...	...
Ash %	62.68	62.95	64.70	...
Loss on ignition %	34.20	34.34	35.30	100.00
Water of carbonization %	2.13	2.14	2.20	6.23
Oil %	11.65	11.70	12.03	34.07
Semicoke %	78.70	79.04	81.25	46.86
Gas and losses %	4.40	4.41	4.52	12.84

^{a}Lab. S. = Laboratory Sample (as received). ^{b}Anal. S. = Analytical Sample (Air dried). ^{c}M.A.F.S. = Moisture and Ash Free Sample.

Table VIII. Specification of the Oil Obtained by Distillation at Low Temperatures for Representative Sample of Q15, Q16, and Q17

(Gebel Hamadat–Gebel Dawi)

Specific gravity 20/4° C.	0.9545 g./ml.	
Fundamental composition:		
Hydrogen %	9.68	
Carbon %	81.84	
Distillation curve:		
Start of the distillation	80° C.	
	110° C.	3 ml.
	160° C.	13.0 ml.
	190° C.	24.0 ml.
	220° C.	35.0 ml.
	250° C.	47.0 ml.
	280° C.	58.0 ml.
	310° C.	68.0 ml.
	350° C.	84.0 ml.
Distillation residue		16.0 ml.

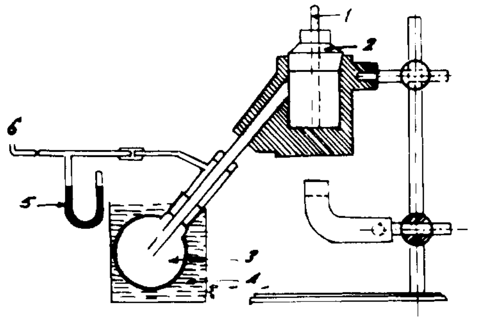

Figure 9. Carbonization at low temperatures

legend:
1 = thermometer,
2 = retort
3 = receiving flask
4 = cooling bath
5 = manometer
6 = collection of gases

Table IX. Analysis of Gas Collected During Carbonization at Low Temperature

	Q 15		Q 16		Q 17	
	%	Net calorific value	%	Net calorific value	%	Net calorific value
Carbon dioxide CO_2	26.11		27.90		24.54	
Unsaturated hydrocarbons C_nH_{2n}	7.00	1076	6.90	988	7.36	1054
Carbon monoxide CO	9.42	284	10.80	326	10.91	331
Hydrogen H_2	32.03	822	30.40	781	33.54	862
Methane CH_4	15.88	1359	14.90	1274	5.73	881
Saturated hydrocarbons C_nH_{2n+2}	5.11	784	4.40	676	12.82	1096
Nitrogen N_2	4.44					
Sum	99.99	4325	100.00	4045	100.00	4224
Volume of gas/1 kg.	35.4 liters		37.1 liters		33.10 liters	

N.B. Net calorific value in kcal./Nm^3.

sumed were all measured. The apparatus was of the conventional volumetric type in which volumes were made comparable by means of pressure-temperature compensator with a manometer interposed between the compensating tube and buret.

The American Society for Testing Materials method, with slight modifications in the determination of oxygen, was used. The gas was bubbled through a pipet containing a solution of 50 grams sodium thiosulfate, 26 grams sodium hydroxide, 10 grams pyrogallic acid, 5 grams anthraquinone, and 300 ml. of distilled water.

This solution gave better results, and was used by the Central Research Institute of Fuels in Prague, since pyrogallic acid in basic medium liberates carbon monoxide which might interfere in the result of analysis.

Results of analyses are given in Table IX. The calculations are described below, using Q15 as the example.

The analysis of gas gave these results

Carbon dioxide	19.4
Unsaturated hydrocarbons	5.2
Oxygen	5.4
Carbon monoxide	7.0
Hydrogen	23.8
Methane	11.8
Saturated hydrocarbons	3.8
Nitrogen	23.6
Sum	100.0

Nitrogen corresponding to air % = $O_2 \times 3.76 = 5.4 \times 3.76 = 20.3$

Actual Nitrogen = 23.6 − 20.3 = 3.3

Volume of air in the gas = 5.4 + 20.3 = 25.7

The determined figures were therefore multiplied by the following factor [100/(100–25.7)], in order to obtain the real values of the constituents of the gas. The net calorific value was calculated according to the last calculated values.

The analysis of gas and calculation of net calorific value:

	Per cent	Net Calorific Value
Carbon dioxide	26.11	...
Unsaturated hydrocarbons	7.00	1076
Oxygen	...	...
Carbon monoxide	9.42	284
Hydrogen	32.04	822
Methane	15.88	1359
Saturated hydrocarbons	5.11	784
Nitrogen	4.44	
Sum	100.00	4325 kcal./Nm.^{3}

INTERPRETATION

The term oil shale applies to a variety of fine grained sedimentary rocks containing organic material which is only slightly soluble in petroleum solvents but is largely converted to oil by application of heat.

Oil shale has been defined by the American Society for Testing Materials as a compact rock of sedimentary origin, with ash content more than 33% and containing organic material that yields oil when destructively distilled but not appreciably when extracted with the ordinary solvents for petroleum.

True oil shale is a fine grained sedimentary rock varying in color from gray or brown or reddish brown to almost black. There is a little outward appearance or feel of oiliness. The Qusseir oil shale is hard rock ranging in color from gray to black. The shale has a distinctive oily odor and the vapors obtained by igniting the shale are white in color. It burns with a rooty flame and petroleum like odor.

The mineralogical examination of Qusseir oil shale showed that it consists of banded clay with disseminated carbonaceous matter and iron oxides; shells of foraminefera are present in notable amounts. The minerals and foraminefera show parallel arrangement similar to that of the banding of the clay. The mineral portion of Colorado (25) carbonaceous shale consists essentially of calcite, clay, quartz, plagioclase and feldspar.

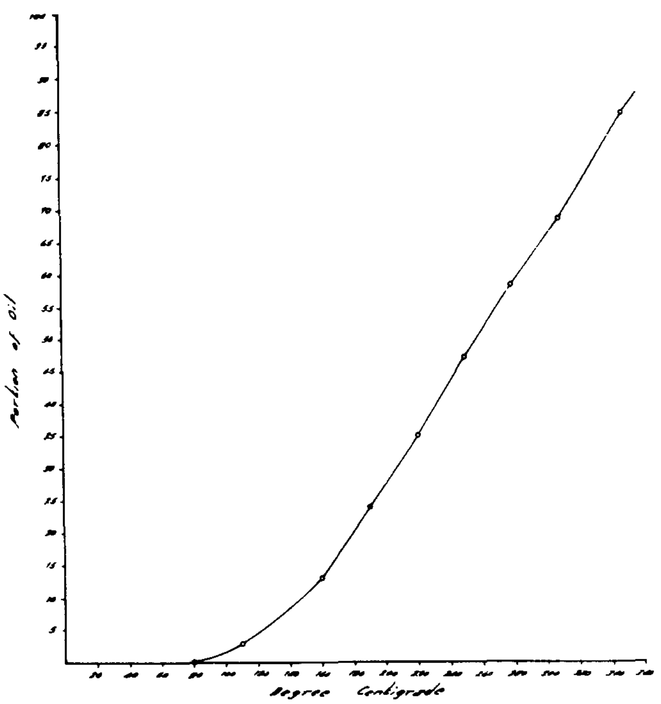

Figure 10. Distillation curve

The sulfur content of Qusseir shale is high if compared with different shales, also the volatile sulfur content is high and ranges from 1.5–1.7. The nitrogen content is similar to that present in Colorado and Australia shale (25).

Locality					
Colorado	Australia	South Africa	Brazil	Spain	Qusseir
		%S			
0.73	0.44	1.01	0.73	1.68	3.6 , 3.81
		%N			
0.44	0.47	0.88	0.50	0.55	0.33, 0.49

The comparison of our data of analysis to that obtained for Volga inflammable shales mined in the U.S.S.R. showed close agreement as is seen in the following table.

C^h	H^h	$S^h_{org.}$	N^h	Q^h_v	A^s	W^p	Q^p_u
			Middle Volga, Kapsis				
61.0	7.5	...	1.2	6950	63.0	14.0	1500
58.7	6.5	...	...	...	...	...	...
			Sabeljev deposit				
61.0	7.7	...	1.1	6950	60.5	20.0	1330
			Qusseir shale				
59.0	7.1	4.8	1.3	5660	64.0	3.1	1790

C^h = the carbon content calculated to dry ash free sample
H^h = the hydrogen content calculated to dry ash free sample
$S^h_{org.}$ = the organic sulfur calculated to dry ash free sample
N^h = the nitrogen content calculated to dry ash free sample
Q^h_v = gross calorific value calculated to dry ash free sample in kcal./kg.
A^s = the ash of the dried sample
W^p = moisture of the laboratory sample
Q^p_u = net calorific value of the laboratory sample in kcal./kg.

Clearly, the results of determinations of calorific value indicate the Qusseir shale is a very low type of fuel. It can be industrialized only under severe conditions of lack of fuels.

The data obtained from the analysis of ash of Colorado shale is similar to the data obtained from the analysis of Qusseir shale. The ash is rich in calcium oxide and could be employed in civil engineering (*7, 27*).

	Locality					
	Colorado	Australia	South Africa	Brazil	Spain	Qusseir
% Ash content	60	45	44	64	63	62 , 64
% SiO_2	42.4	90.7	60.6	58.0	56.6	34.47, 37.2
% Fe_2O_3	4.7	0.9	3.1	8.5	9.1	4.25, 7.62
% Al_2O_3	10.5	4.8	30.4	24.5	27.7	10.26, 11.12
% CaO	23.5	0.5	1.9	2.6	2.6	26.52, 27.9
% MgO	9.3	0.3	1.7	3.3	2.2	1.54, 2.06
% SO_3	2.0	6.2	0.1	0.7	0.5	6.85, 8.86
%^{a} Misc.	7.6	2.6	2.2	2.4	1.3	about 11

^{a} Misc. represents mainly the alkali metals, sodium and potassium. The following elements have been reported B, Ba, Be, Bi, Ag, As, Au, Co, Cr, Cu, Ng, Ir, Mn, No, Ni, P, Pb, Sb, Se, Sn, Ti, Tl, U, V, and Zn.

The per cent phosphorous calculated as P_2O_5 in the Qusseir shale ranges from 3.5 to 4.8. The titanium dioxide content is about 0.5.

The spectrographic analysis of the Qusseir shale showed that Zn, Cr, Cu, Mo, V, Ag, B, Cd, Ba, Ni, Ga, Sn, Pb, and Yb are present in trace amounts.

The organic material in the oil-shale is frequently called kerogen and its content is normally up to 25%. Very little is known about kerogen although obviously it is not a single chemical compound but a complex mixture of organic compounds which vary greatly in different oil shales (*25*). According to Cane (*25*), kerogen is a noncrystalline substance, possibly a polymer of high molecular weight consisting of cyclic nuclei with long and short side chains and numerous cross linkages. Studies are in progress to determine the constitution of kerogen as a means of devising more suitable methods for its conversion to shale oil.

We attempted to get complete analytical data for the volatile organic matter as data indicated that the efficiency of the conversion to oil depends on the character of the organic material and to a lesser extent on the amount and character of the associated mineral matter in the shale.

The organic content of the Qusseir shale was determined according to the described detailed method, and showed little difference from the approximated figures, obtained by subtracting the mineral carbon dioxide from the ignition loss of the shale.

Sample	Organic Content	Approximated Figures
Qusseir carbonaceous shale (*15*)	21.08	21
Qusseir carbonaceous shale (*16*)	21.75	20.8
Qusseir carbonaceous shale (*17*)	22.21	22.7

The classical conception of the conversion reaction of kerogen (*26*) to oil, gas, and coke is that it is a depolymerization, in which first a solid or semisolid bitumen is formed and then by the cracking of this primary product oil, gas, and coke result. Although the basic reaction is not yet fully understood, it was clear experimentally that the organic material with the highest carbon to hydrogen ratio yielded the least oil. The C:H ratio of Qusseir's carbonaceous shale ranges from 8–10 (*25*).

The C:H content of different representative samples

Colorado	5.6	7.1	7.0	7.8	7.6
Australia	7.8	8.1	11.5		
South Africa	8.7	9.8	11.1	12.4	
Brazil	6.3				
Spain	8.3				
Qusseir shale	8.3	8.7	10.2		

In Soviet Standards GOST 3144–46, the minimum output of tar obtained by carbonization at low temperatures is normalized to 10% for the dry sample with maximum ash content of 60%. These conditions are comparable with that obtained by the analysis of Qusseir's carbonaceous shales.

The per cent tar in the Qusseir shale ranges from 10.8–12 with ash content 63–66% for the dry sample.

Shale oil, like petroleum, is composed of hydrocarbons and sulfur, nitrogen, and oxygen derivatives of hydrocarbons. Unlike petroleum, however, it contains large quantities of unsaturated hydrocarbons and heterocyclic compounds (*26*). Although the crude oil is relatively stable, distillates prepared from it exhibit definite instability. The shale oil differs both because of different oil shales and because of retorting methods (*8*). The degree of aromaticity is high as shown by C:H ratio; 7 is about normal for shale oils and low by comparison with coal carbonization products (from 9–18).

The C:H value in the Qusseir shale oil is 8.45, obtained from the ultimate analysis of the oil obtained by carbonization at low temperatures. For the sake of comparison, the C:H ratio for shale oils in different localities is given below.

Locality and Type of Retorting	C:H ratio
United States, N-T-U	7.35
Australia, pumpherston	7.14
Spain, pumpherston	7.21
France, pumpherston	7.6

The distillation curve shows that this kind of tar contains 44% petroleum fraction 110–250° C. A small extract of benzin 3%, up to 110° C. may be explained by the fact that the loss of low boiling fractions during our distillation of small amounts of the sample was comparatively high (*17, 23*).

The deficiency in low boiling material and the presence of S and N compounds indicate some of the problems in preparing fuels.

Heavy gas oil distillate (*19*), the counterpart of petroleum wax distillate, yields a considerable amount of crude wax, by solvent extraction. Tar acids and tar bases are recoverable in considerable quantity from shale oil. Viscous and asphaltic residues are also obtained from crude shale oil. These are the subject of the next work.

The gas obtained by carbonization at low temperature is rich in hydrogen ranging from 30–34%, within the range of 4046–4235 kcal./Nm^3. This carbonizing gas represents a good quality of gaseous fuel that may be widely used after washing in carbon dioxide which is contained in the raw gas by 24.5–27.9%.

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Preparation of 1,1′- and 5,5′-Bitetralyl

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The preparation of 5,5′-bitetralyl (m.p. 93.5–94° C.) by the partial hydrogenation of 1,1′-binaphthyl using a palladium-on-carbon catalyst is described. The main product from the reaction of di-*tert*-butyl peroxide with tetralin (1,2,3,4-tetrahydronaphthalene) is 1,1′-bitetralyl. The identity of the bitetralyls was confirmed by elemental analysis, NMR spectrum, and, in the case of the 1,1′ isomer by dehydrogenation to 1,1′-binaphthyl. The presence of *meso* and *racemic* stereoisomers of 1,1′-bitetralyl was demonstrated.

IN THE COURSE of some studies on the radiolysis of 1,2,3,4-tetrahydronaphthalene (tetralin), two bitetralyls were prepared as standards to aid in the analysis of the polymer. One of these, 5,5′-bitetralyl, had not been described previously and was prepared by the partial hydrogenation of 1,1′-binaphthyl. The other , 1,1′-bitetralyl, had been isolated as a by-product from a Grignard reaction involving 1-bromotetralin (*3*). A more convenient preparative method was to treat tetralin with di-*tert*-butyl peroxide. This is similar to a published method of dimerizing alkylbenzenes using diacetyl peroxide (*1*).

EXPERIMENTAL

Preparation of 5,5′-Bitetralyl. Ten grams of 1,1′-binaphthyl (Aldrich Chemical Co.) in 90 grams of cyclohexane plus two grams of 5% palladium-on-carbon catalyst was hydrogenated in a Paar hydrogenation apparatus at an initial pressure of 40 p.s.i.g. and 65–70° C. After 24 hours an additional two grams of catalyst was added and hydrogenation continued for another 24 hours after repressuring the system to 40 p.s.i.g. The crude hydrogenation product was absorbed on 135 grams of silica gel. Elution with *n*-pentane gave no high boiling eluate, indicating that no bidecalyl was formed. Using benzene, nine grams of eluate was recovered which, upon several recrystallizations from absolute alcohol, gave 5.2 grams of colorless crystals melting at 93.5–94° C. (no literature value reported.) *Anal.*Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.35; H, 8.38.

This isomer differs from 1,1′-bitetralyl in melting point, mass spectrum, and NMR specturm. In the NMR spectrum, there were four fully resolved proton peaks corresponding to aromatic protons (δ = 6.84 ppm), 4,4′ protons (δ = 2.74 ppm), 1,1′ protons (δ = 2.26 ppm), and combined 2,2′ and 3,3′ protons (δ = 1.66 ppm). The observed areas were in the ratio 5.8 : 4.0 : 3.6 : 7.5, which agree very well with the calculated values 6:4:4:8. Analysis of the spectra leading to values of the various coupling constants is not possible due to the poorly resolved structure within the assigned regions of the spectrum.

Preparation of 1,1′-Bitetralyl. A mixture of 132 grams (1.0 mole) of tetralin and 14.6 grams (0.1 mole) of di-*tert*-butyl peroxide was heated in helium atmosphere to 155° C. in a flask equipped with a Dean-Starke type of distilling tube receiver and a reflux condenser. Reflux started shortly thereafter as *tert*-butyl alcohol was formed. When the temperature reached 135° C., the alcohol and some peroxide were removed. The temperature was raised to 155° C. again during this distillation. The total distillate was 8.0 ml. of which 6.5 ml. was *tert*-butyl alcohol. A volume of peroxide equal to the total volume of distillate was added to the reaction mixture and the cycle was repeated. After collecting 26.5 ml. (ca. 0.3 mole) of the alcohol in this manner, the reaction mixture was distilled in a Piros-Glover spinning band column at 10mm. Hg pressure. Thirty grams of a clear, viscous liquid boiling at 223° C. was obtained, and, upon standing, it partially crystallized. Recrystallization from absolute alcohol gave colorless crystals melting at 82° C. [lit. value 83° C. (*3*)]. *Anal.* Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.60; H, 8.42.

The NMR spectrum showed proton peaks corresponding to aromatic hydrogens (δ = 6.97 p.p.m), tertiary hydrogens (δ = 3.37 p.p.m), secondary hydrogens on alpha carbon atoms (δ = 2.65 p.p.m); and secondary hydrogens on beta carbon atoms (δ = 1.77 p.p.m). The observed areas were in ratio 8.9 : 2.4 : 4.1 : 7.5, which are in good agreement with the calculated values 8:2:4:8. J-values could not be determined for the same reason cited under the previous preparation.

Dehydrogenation of the product with palladium-on-