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The Nature of Sulphur Compound Types in Bakr Crude Oil

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With 6 Figures

Abstract

A detailed analytical scheme for the determination of different sulphur compound types in Bakr crude oil distillate fractions up to 350 °C was carried out. The quantitative distribution of elemental sulphur, hydrogen sulphide, mercaptans, aliphatic sulphides, aromatic sulphides, reducible and thiophenic sulphur compound types was studied.

Introduction

Egyptian crude oils contain a relatively high percentage of sulphur ranging from 2.0 to 4.5% with the crude oil from the Bakr oilfields topping them all, Table 1.

Research on the types of sulphur compounds found in Egyptian crude oils is relatively recent and a much deeper insight with respect to the distribution of the different types of sulphur compounds throughout the whole crude is needed in order to devise practical desulphurization methods applicable to each individual crude oil and its respective fractions.

The variety of sulphur compounds that may be present in petroleum is enormous and their identification is difficult because they are only found in relatively very small quantities. Most of the sulphur is associated with the higher boiling fractions especially with the resins and asphaltenes where they act as bridges between the aromatic rings present or as part of the ring structures.

Experimental

A sample of blended crude oil from the Bakr Oilfields, was fractionally distilled under 5 mm. Hg. pressure into 10 °C cuts whose physical characteristics are given in Table 2. Hydrogen sulphide and light distillates were collected in two dry ice traps from whence, at the completion of the experiment, the hydrogen sulphide was vaporized by warming at room temperature, bubbled into a sodium hydroxide solution and determined potentiometrically.

Table 1
Bakr crude oil characteristics compared with that of Land Belayeem, Marine Belayeem and Ras Gharib Crude Oils

	Bakr	Marine[a]) Belayeem	Land[b]) Belayeem	Ras[b]) Gharib
Sp. Gr. 15/4 °C, I.P. 160	0.9250	0.8815	0.9210	0.9050
API gravity at 60 °F	21.4	29.02	22.14	24.85
Sulphur content wt. % I.P. 63	4.15	2.00	3.08	3.07
Water content I.P. 174	0.02	Nil	0.3	0.3
Engler viscosity at 20 °C, sec.	38	3.64	33.3	13.4
Pour Point °F, I.P. 15	30	50	30	30
Carbon residue (wt. %) I.P. 13	10.3	5.5	10.6	8.5
Ash content wt. % I.P. 4/65	0.02	0.01	0.047	0.05
Asphaltenes wt. % I.P. 6	13.5	4.0	9.41	6.8
Distillation I.P. 24:				
I.B.P. °C	58	48	75	68
Vol.-% recovery to 75°	2.0	4.0	—	—
100°	3.0	7.0	4.0	4.0
125°	5.0	10.0	7.0	7.5
150°	8.0	15.0	10.5	11.5
175°	13.0	19.0	14.0	15.0
200°	15.0	24.0	17.0	19.0
225°	18.0	26.0	20.0	23.0
250°	22.0	30.0	23.5	26.0
275°	26.0	35.0	27.5	31.0
300°	30.0	40.0	32.0	35.0
Residue %	69.0	59.0	67.0	64.0
Loss	1.0	1.0	1.0	1.0
Total	100.0	100.0	100.0	100.0

[a]) Analytical data from El Fayoumi, G. F. (M. Sc. Thesis). Cairo Univ.
[b]) Analytical data from Borham, M. A. (Ph. D., 1960). Cairo Univ.

Determination of sulphur compound types

The scheme used for the sulphur group analysis is the one described by Rubinshtein et al.[1]) with slight modifications where determinations of mercaptans and disulphides in the gasoline boiling range were concerned. This method is based on straight potentiometric titrations of different groups of sulphur compounds in the presence of each other. Primary qualitative tests indicated the absence of free sulphur and hydrogen sulphide from all distillate fractions, hence no quantitative estimations were carried out.

1. Determination of mercaptans

The method consists in the argentimetric estimation of mercaptans by means of potentiometric titration using silver sulphide and calomel electrodes. For samples in the gasoline

[1]) I. A. Rubinshtein, Z. A. Kleimenova and E. P. Sobolev, Metoda Analiza, Organ Soeden, Neft. Ikh Smesei i Projo. Akad. SSSR, Inst. Neftekhem. Suiteza, Sb. No. 1, 74 (1960).

Table 2
Physical Constants and Total Sulphur Content of the 10°C Vacuum Distillate Fractions of Bakr Crude Oil

Fraction No.	Boiling range °C	% by wt. in crude	Refractive index n_D^{20}	Density d_4^{20}	Total sulphur content % wt.	% total sulphur to crude
1	32—50	0.022	1.3955	0.6940	0.073	0.00038
2	50—60	0.034	1.4016	0.6960	0.086	0.00069
3	60—70	0.046	1.4025	0.7010	0.087	0.00095
4	70—80	0.064	1.4031	0.7050	0.097	0.00140
5	80—90	0.098	1.4042	0.7190	0.155	0.00360
6	90—100	0.128	1.4065	0.7200	0.180	0.00540
7	100—110	0.116	1.4095	0.7277	0.192	0.00530
8	110—120	0.330	1.4119	0.8326	0.245	0.01900
9	120—130	0.382	1.4171	0.7439	0.256	0.02300
10	130—140	0.508	1.4235	0.7535	0.284	0.03400
11	140—150	0.437	1.4255	0.7606	0.471	0.04900
12	150—160	0.807	1.4305	0.8187	0.411	0.07800
13	160—170	0.553	1.4310	0.7613	0.548	0.07200
14	170—180	0.780	1.4395	0.7918	0.675	0.12700
15	180—190	1.013	1.4348	0.7772	0.780	0.18800
16	190—200	0.875	1.4429	0.7905	0.827	0.17200
17	200—210	0.736	1.4524	0.8302	1.098	0.19200
18	210—220	0.657	1.4490	0.8083	1.112	0.174
19	220—230	0.606	1.4552	0.8589	1.197	0.172
20	230—240	0.872	1.4520	0.8120	1.245	0.259
21	240—250	0.829	1.4573	0.8193	1.267	0.250
22	250—260	0.899	1.4576	0.8179	1.312	0.280
23	260—270	1.038	1.4645	0.8338	1.700	0.386
24	270—280	1.297	1.4640	0.8392	1.556	0.480
25	280—290	1.090	1.4705	0.8387	1.638	0.424
26	290—300	1.068	1.4751	0.8452	2.193	0.557
27	300—310	1.055	1.4781	0.8597	2.227	0.559
28	310—320	1.040	1.4788	0.8797	2.234	0.552
29	320—330	1.062	1.4789	0.8569	2.320	0.585
30	330—340	1.051	1.4769	0.8557	2.526	0.631
31	340—350	1.140	1.4805	0.8579	2.538	0.688

boiling range application of this procedure did not give rise to a potential difference and the fraction had to be shaken with a silver nitrate solution and the unreacted silver nitrate titrated against standard ammonium thiocyanate solution using ferric alum as indicator.

2. Determination of total sulphides

The procedure consists in completely dissolving the samples in a solution of glacial acetic acid benzene, and hydrochloric acid which is then potentiometrically titrated against potassium iodate solution using platinum and calomel electrodes.

3. Determination of aliphatic sulphides

This was effected by spectrophotometric determination measuring the absorption caused by iodine — aliphatic sulphide complexes at 310 mμ on a BECKMAN DU spectrophotometer according to the procedure described by HASTINGS[2]) and DRUSHEL[3]).

4. Determination of total reducible sulphur

Both disulphides and polysulphides were determined by their reduction in glacial acetic acid and powdered zinc to mercaptans by a procedure described by RUBINSHTEIN et al.[1]) with a slight modification to prevent the loss of low boiling mercaptans during reduction.

5. Determination of thiophens

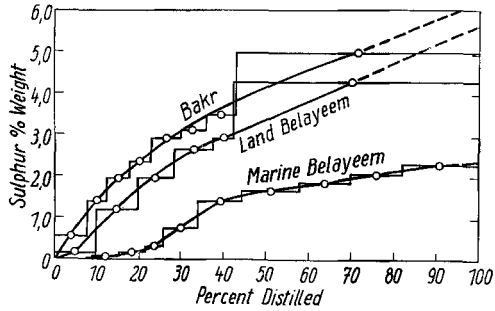
The method of MCCOY and WEISS[4]) with MARTIN and GRANT's modification[5]) was used, which essentially consists of catalytically decomposing all sulphur compound types except thiophenes in a quartz tube at 500 °C and the potentiometric determination of the hydrogen sulphide and mercaptans produced and calculating the thiophene content by difference.

Results and Discussion

General Characteristics of Bakr crude oil.

Compared with other main producing oilfields crudes from the Bakr oilfield are characterized by having the highest sulphur, asphaltene and resin contens, Table 1. As regards the type of crude, all indigenous crude oils including Bakr crude are of the mixed type being of the paraffinic, naphthenic aromatic class of the waxy, asphaltic, sulphurous group.

Compared with marine and land Belayeem crude oils, the sulphur content of Bakr crude oil fractions, as weight percent, increases sharply with



F'g. 1. Relationship between percent sulphur and percent distilled in Bakr and Belayeem crude oils

[2]) S. H. HASTINGS, Z. analyt. Ch. **25**, 420 (1953).

[3]) H. V. DRUSHEL and J. F. MILLEE, Z. analyt. Ch. **27**, 495 (1955).

[4]) R. N. MCCOY and F. T. WEISS, Z. analyt. Ch. **26**, 1928 (1954).

[5]) R. L. MARTIN and J. A. GRANT, A.C.S. Preprints. Pet. Chem. 10, No. 2, April, 1965, Detroit, Michigan.

Table 3
Sulphur Type Distribution in the 10°C. Vacuum Distillate Fractions of Bakr Crude Oil

Fraction No.	Boiling range °C	Total sulphur wt. %	Total R.S.H.	$\frac{RSH}{s} \times 100$	Total RSR_1	$\frac{RSR}{s} \times 100$	Aliphatic sulphides RSR_1	$\frac{RSR_I}{s} \times 100$	Aromatic sulphides*)	Total reducible sulphur $RSS_x R$	$\frac{RSS_X R}{s} \times 100$	% residual sulphur
1—7	1—110	0.212	0.0036	1.71	0.045	21.3	0.044	21.2	—	—	—	77.0
8	110—120	0.245	0.0056	2.29	0.067	27.3	0.065	27.1	—	—	—	70.4
9	120—130	0.256	0.0086	3.37	0.140	54.6	0.140	54.6	—	—	—	42.0
10	130—140	0.284	0.0035	1.23	0.229	80.6	0.228	80.6	—	0.008	2.80	15.4
11	140—150	0.471	0.0024	0.72	0.308	65.4	0.308	65.4	—	0.008	1.70	32.2
12	150—160	0.411	0.0037	0.30	0.266	64.7	0.265	64.7	—	0.007	1.70	32.7
13	160—170	0.548	0.0050	0.91	0.266	48.5	0.261	48.4	0.1	0.006	1.09	49.5
14	170—180	0.675	0.0140	2.07	0.379	56.1	0.379	56.1	—	0.006	0.90	40.9
15	180—190	0.780	0.0680	9.51	0.655	83.9	0.650	83.8	0.1	0.007	0.89	5.8
16	190—200	0.827	0.0580	7.01	0.719	86.9	0.710	86.4	0.5	0.008	0.96	5.2
17	200—210	1.098	0.0340	3.09	0.780	71.0	0.512	46.7	24.3	0.009	0.81	25.1
18	210—220	1.112	0.0420	3.78	0.734	66.0	0.690	62.0	4.0	0.010	0.89	29.3
19	220—230	1.197	0.0300	2.50	0.914	76.3	0.800	66.7	9.6	0.002	0.16	20.1
20	230—240	1.245	0.0227	1.82	1.173	94.2	0.940	75.5	18.7	0.010	0.80	3.2
21	240—250	1.267	0.0280	2.20	1.180	93.1	0.502	39.6	53.5	0.012	0.95	4.8
22	250—260	1.312	0.0280	2.13	1.238	94.3	0.487	39.4	54.9	0.014	1.06	2.5
23	260—270	1.700	0.0180	1.05	1.416	83.3	1.120	65.8	17.5	0.020	1.18	14.5
24	270—280	1.556	0.0050	0.33	1.300	84.2	1.200	77.1	7.1	0.028	1.82	13.7
25	280—290	1.638	0.0036	0.22	1.472	89.8	0.850	51.8	38.0	0.040	2.44	7.5
26	290—300	2.193	0.0049	0.22	1.396	63.7	1.090	49.7	14.0	0.062	2.82	33.4
27	300—310	2.227	0.0053	0.23	1.513	67.9	0.370	16.3	51.6	0.064	2.87	29.0
28	310—320	2.234	0.0039	0.17	1.416	63.3	1.210	54.1	9.2	0.058	2.59	34.0
29	320—330	2.320	0.0052	0.22	1.256	54.1	0.740	31.8	22.3	0.055	2.37	43.3
30	330—340	2.526	0.0044	0.17	1.525	60.4	0.580	11.0	49.4	0.064	2.53	36.9
31	340—350	2.538	0.0035	0.13	1.238	48.7	1.140	44.9	3.8	0.057	2.24	49.0

*) Aromatic sulphides calculated by difference between total sulphides and aliphatic sulphides.

increasing yields of distillate fractions, so that when the curves are extrapolated to 100% distilled the sulphur contents of the residual fractions amount to 4.8% (Fig. 1).

Assuming that:

1. The mean molecular weight of the sulphur compounds in any one fraction is the same as that of the material distilling within the boiling range of the fraction.

2. Only one atom of sulphur is contained in each sulphur compound molecule. A curve is obtained for Bakr crude oil (Fig. 2), that indicates that this oil contains more than 50% sulphur compounds and that the last

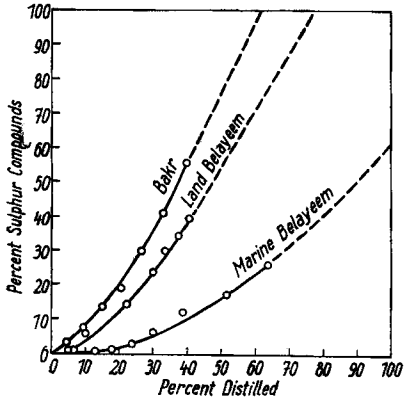


Fig. 2. Relationship between percent sulphur compounds and percent distilled in Bakr, land Belayeem and marine belayeem crude oils

50% of the crude oil consists entirely of sulphur compounds. Additionally as the curve passes off the chart at approximately 60% distilled, it is apparent that some of the sulphur compounds contain two or more sulphur atoms.

Bakr crude oil is not unique in this respect, Heidelberg crude oil of California exhibits the same characteristics[6]).

Marine Belayeem however, with a total sulphur content of 20% contains only a maximum of 55% sulphur compounds at 100% distilled and land Belayeem with a total sulphur content of 30% lies between the 2 extremes.

From the analyses carried out on the 10 °C distillate fractions (Table 3), the following are shown.

1. Sulphides constitute the main bulk of the sulphur types present in the distillate fractions up to 350 °C.

[6]) H. T. Rall, C. J. Thompson, H. J. Coleman and R. L. Hopkins, Proc. A.P.I. 42 (VIII), p. 19–27 (1962).

2. The distribution of mercaptans differs from one fraction to another (Fig. 3), the curve showing two maximum peaks in the boiling ranges 120° to 130 °C and 180—190 °C, above 200 °C the distillate fractions contain negligible amounts of mercaptan sulphur.

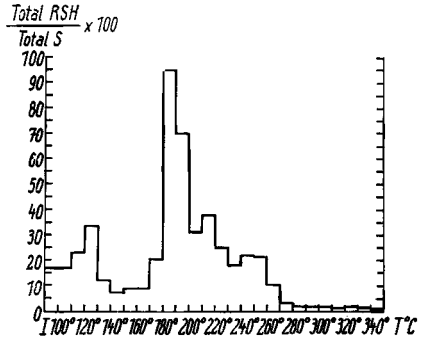


Fig. 3. Distribution of mercaptan in relation to total sulphur in the 10 °C fractions of Bakr crude oil

3. From Fig. 4 it is clearly shown that the sulphide sulphur contents below 120 °C are relatively low, the balance appearing mainly as residual sulphur. Above 120 °C the sulphide sulphur content increases sharply and starting from 300—320 °C the concentration of sulphide sulphur starts to decrease.

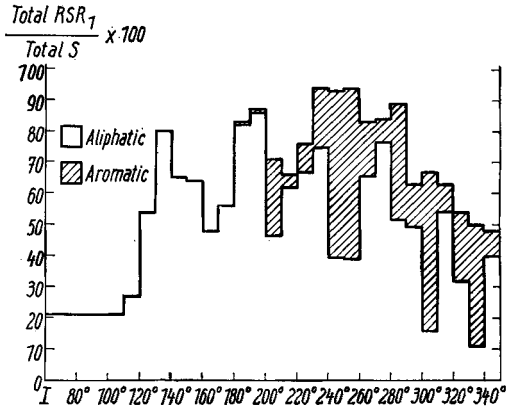


Fig. 4. Distribution of sulphides in relation to total sulphur in the 10 °C fractions of Bakr crude oil

4. Up to a boiling point of 200 °C the sulphide sulphur appears as aliphatic sulphur compounds, the concentration of aromatic sulphides starts to increase changing from one fraction to another and constituting in some fractions more than 80% of the total sulphide sulphur contract.

5. With regard to the content of reducible sulphur, Fig. 5 demonstrates the scarcity of reducible sulphur in the distillate fractions up to 130 °C.

The reducible sulphur content increases suddenly to a maximum in the fraction boiling at 130—140 °C decreases rapidly again to a minimum in the fractions of 210—220 °C boiling range, then increases again to a maxima in the 290—310 °C boiling range.

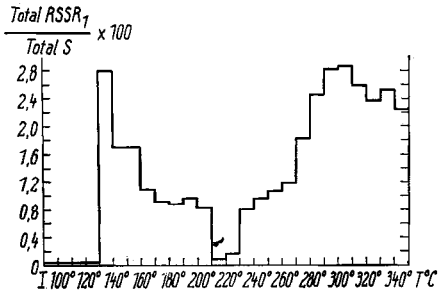


Fig. 5. Distribution of reducible sulphur in relation to total s in the 10 °C fractions of Bakr crude oil

6. With respect to the residual sulphur content, there are big variations from one fraction to another, yet, unexpectedly the highest residual sulphur content lies in the lightest fractions (1—110 °C), (Fig. 6).

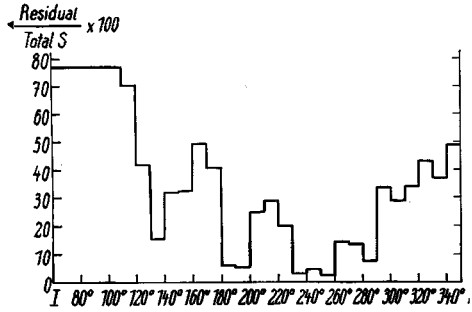


Fig. 6. Distribution of residual sulphur in relation to total sulphur in the 10 °C fractions of Bakr crude oil

As the sulphur type analysis of the 10 °C fractions has been carried out under fractionation conditions practically excluding any cracking or oxidation reactions, the picture of the sulphur type analyses obtained is more or less representative of the actual sulphur type distribution.

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