

## SULPHUR COMPOUNDS IN LIGHT ARABIAN AND KUWAIT CRUDE OILS

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**Abstract.** The sulphur compounds in petroleum, both as to type and quantity, have long been of concern to the refiners due to their corrosiveness, disagreeable odour, deleterious effects on colour or colour stability, and unfavourable influence on antiknock and oxidation characteristics. A systematic study of the distribution of sulphur compounds in crude oils is not only of theoretical interest, but also of practical value to petroleum industry.

A study of the type of sulphur compounds present in light Arabian and Kuwait crude oils distillates up to 600°F has been carried out. The sulphur type distribution of the following types of sulphur compounds is discussed: hydrogen sulphide, elemental sulphur, mercaptans, aliphatic sulphides, aromatic sulphides, disulphides and residual sulphur.

## Introduction

All known crude oils contain sulphur compounds which, analyzed as per cent total sulphur may vary in quantity from below 0.05 to about 5.0% weight or more. Sulphur compounds are commonly considered objectionable in finished oils because of their actual or potential corrosiveness, disagreeable odour, deleterious effect on colour or colour stability, and unfavourable influence on antiknock and oxidation characteristics.

The distribution of sulphur in various fractions of crude oils has been studied many times and various types have been identified. The most comprehensive study was done under API Research Project 48 on the synthesis, properties and identification of sulphur compounds. The sulphur compounds of Wassen, Texas, Wilmington, California and Agha Jari crude oils have been described in U.S. Bureau of Mines bulletin 659 [1]. Birch *et al.* [2] have studied the sulphur compounds in kerosene fraction from mixed Iranian crude oils. The nature and distribution of sulphur compounds in Agha Jari straight run naphthas has been discussed by Hale *et al.* [3]. Ahmed *et al.* [4] have published their study on sulphur compounds types in Baker crude oil from Egypt. Recently Agrawal *et al.* [5] have studied the sulphur compounds found in Darius crude oil distillates upto 350°C.

This paper is concerned with the study of sulphur compounds found in Light Arabian and Kuwait Crude Oils distillates up to 600°F. Both Light Arabian and Kuwait crude oils are fairly high in sulphur, respectively. Five distillate cuts were obtained from laboratory batch fractionation using a True Boiling Point Distillation apparatus. These distillate cuts were fully studied for the type and concentration of various sulphur groups likely to be present.

## Experimental

**Preparation of Distillate Cuts.** The properties of light Arabian and Kuwait Crude oils used for this

study are given in Table I. The distillation of crude oil was carried out using a podbielniak TBP distillation apparatus having a 25-mm diameter, vacuum jacketed, 36-inch long fractionating column packed with "Heli-Pak", packing, at a reflux ratio of 5:1. Five distillate fractions, the first one up to 200°F and the other four fractions at 100°F intervals up to 600°F were collected. The properties of these cuts are given in Table 2.

**Methods of Analysis.** The following types of sulphur compounds were determined quantitatively in the distillate fractions using the following methods of analysis.

**Hydrogen Sulphide and Mercaptan Sulphur.** Hydrogen sulphide and mercaptan sulphur were determined potentiometrically [6] in an alcoholic solution of sodium acetate using alcoholic silver nitrate as titrant. A glass reference electrode and a silver-silver sulphide indicating electrode system was used. Estimation was made from inflections in titration curves. The inflection for sulphide ion and mercaptate ion were observed respectively at EMF +0.4V and -0.1V. Elementary sulphur, if present, could also be determined by this method.

Duplicate results by the same tester should not differ by more than 0.0004%.

**Disulphides and Total Sulphides.** The disulphide and total sulphide contents in the distillates were determined by removing mercaptans initially present in the samples, the disulphides were reduced to mercaptans and hydrogen sulphide by refluxing in the presence of acid and zinc. These were titrated with silver nitrate [7] and removed from the sample. Total sulphur was then determined [8] on the treated sample before and after shaking with mercurous nitrate. The sulphur removed by the mercurous nitrate was reported as the sulphide sulphur in the sample.

For disulphide sulphur duplicate results by the same tester should not differ by more than 0.0004%; and for total sulphur the duplicate results should not differ by more than 0.005.

**Aliphatic Sulphides.** Aliphatic sulphides were determined by a spectrophotometric method [9] using a Beckman DBG spectrophotometer. This

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TABLE 1. CHARACTERISTICS OF CRUDE OILS.

Crude Oil	Light Arabian	Kuwait
API gravity	33.5	31.4
Conradson carbon % wt	3.8	5.86
B.S. & W% vol.	0.1	50.05
Hydrogen sulphide PPM	16.0	73.0
Pour point °F	Below zero	Below zero
Salt, lbs 1000 bbl.	4.0	3.0
Total sulphur %wt	1.61	2.5
RVP, lb @ 100 °F	4.9	8.2
Viscosity SUS at 100 °F	44.5	58.0
Distillation (ASTM D-285)		
% Recovery °F		
IBP	80.0	88.0
3 1/3	124.0	146.0
6 2/3	174.0	199.0
10	224.0	234.0
13 1/3	254.0	270.0
16 2/3	282.0	298.0
% Recovery at 300 °F	18.3	16.6

method is based upon the formation of intermolecular complexes of aliphatic sulphides and iodine having maximum absorption at about 310 nm.

Duplicate results by the same Operator should not differ by more than 0.008.

*Aromatic Sulphides.* Aromatic sulphides were calculated by difference from the values obtained for total sulphide and aliphatic sulphides.

*Elemental Sulphur.* Elementary sulphur was determined by a spectrophotometric method based on the reaction of free sulphur with cyanide-ferric chloride reagent [10]. The intensity of the coloured ferric-thiocyanate complex formed was measured at 480 nm.

Duplicate results by the same operator should be considered suspect if they differ by more than 0.008.

*Total Sulphur.* The total sulphur content was determined by the lamp method [8]. The duplicate results by this method should not differ by more than 0.005.

*Residual Sulphur.* The difference between total% sulphur and the sum of % elemental sulphur, hydrogen sulphide, mercaptans, sulphides and, disulphide sulphur compounds was reported as residual sulphur.

TABLE 2. GENERAL CHARACTERISTICS AND TOTAL SULPHUR CONTENT OF DISTILLATE FRACTIONS EX. LIGHT ARABIAN (LA) AND KUWAIT (KU) CRUDE OILS.

Fraction	Boiling range (°F)	Yield % wt				Sp. gr. 60/60 °F	Colour	RI @20°C		Total sulphate % wt		Total sulphur as % of total sulphur in cut	
		On crude	Cummulative	LA	Ku			LA	Ku	LA	Ku	LA	Ku
	Gas and loss below 80°	3.0											
1	80-200	5.37	8.37	9.9	0.6822	+30	1.3844	1.3923	0.024	0.019	0.077	0.039	
2	200-300	8.63	17.0	17.4	0.7342	+30	1.4020	1.4130	0.041	0.027	0.211	0.08	
3	300-400	8.55	25.55	25.8	0.7798	+30	1.4258	1.4363	0.150	0.092	0.767	0.31	
4	400-500	7.67	33.22	33.7	0.8038	+22	1.4398	1.4526	0.244	0.32	1.14	1.005	
5	500-600	10.59	43.81	42.4	0.8378	L1.0	1.4660	0.4686	0.664	1.29	4.34	4.45	
6	600+	56.19	100.0	100.0	0.9342	Dark black	*	*	2.7	4.09	93.3	93.60	

\* Sample too dark for RI reading.

TABLE 3. SULPHUR COMPOUNDS IN DISTILLATION FRACTIONS OF LIGHT ARABIAN AND KUWAIT CRUDE OIL.

Fraction	Boiling range (°F)	Sulphur Types as percent wt. of Total Sulphur in cut																	
		Total sulphur % wt.		Hydrogen sulphide		Elemental sulphur		Mercaptans (RSH)		Total sulphide		Aliphatic sulphide (R-S-R-I)		Aromatic sulphide (R-S-R-II)		Disulphide (R-S-S-R)		Residual sulphur	
		LA	Ku	LA	Ku	LA	Ku	LA	Ku	LA	Ku	LA	Ku	LA	Ku	LA	Ku	LA	Ku
1	80-200	0.024	0.019	+	4.2	+	0.5	70.5	15.8	6.0	1.0	1.2	14.8	4.8	20.8	17.4	8.4	1.4	
2	200-300	0.041	0.027	+	3.7	+	0.5	52.2	28.4	13.3	3.6	4.5	24.8	8.8	10.2	8.9	18.6	21.1	
3	300-400	0.15	0.092	0.3	1.6	0.04	0.2	8.4	31.26	16.3	4.3	6.6	26.96	9.7	7.2	5.0	55.9	68.5	
4	400-500	0.244	0.32	+	0.16	+	+	0.9	33.0	28.1	5.7	9.4	27.3	18.7	0.8	0.2	63.8	70.64	
5	500-600	0.664	1.29	*	*	*	*	1.0	31.5	29.0	*	*	*	*	0.2	+	67.3	71	
6	600+	2.70	4.09	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	

+ Below detectable limits

\* Not done

## Results and Discussions

The distillate yields as obtained from TBP fractionation are moderately high for both crudes; at a temperature of 600° F the yields are 43.8 and 42.4% weight respectively for light Arabian and Kuwait crude oils.

The total sulphur content as obtained in the different distillate fractions of light Arabian and Kuwait crude oils are reported in Table 2. This shows a general increase in the sulphur contents of distillate fractions with their boiling point for both crude oils.

The analysis of the distillate fractions from light Arabian and Kuwait crude oils for various type of sulphur groups (Table 3) are discussed as follows:

Hydrogen sulphide and elemental sulphur were found in the lower distillate fractions boiling up to 400°F, beyond this temperature these are present in negligible amount. The presence of elemental sulphur in the initial cuts (naphtha) has been reported by other workers[1,5] in Heidelberg, Oregon Basin, Agha Jari, Wasson, Kirkuk and Darius Crude Oils.

The sulphur as mercaptan sulphur was the chief constituent in the first two distillate fractions boiling up to 300°F. The mercaptan contents in light Arabian crude distillate fractions was higher than in the corresponding Kuwait crude fractions but the per cent ratio of total sulphur in cut for Kuwait distillates was high as compared to light Arabian distillate fractions. The mercaptans in the high boiling fractions were found to decrease rapidly to an almost negligible amount in 500 to 600°F fraction.

The sulphides and disulphides are the most important sulphur compounds present in the crude oil distillate fractions as they constitute the greater part of the sulphur compounds present throughout the boiling range. In the analysis of these crude oils the total sulphides are segregated into aliphatic sulphides (R-S-R-I) and aromatic sulphides (R-S-R II). Generally the total sulphide contents in both light Arabian and Kuwait crude fractions were found to increase with an increase in the boiling point.

The total reducible sulphur is reported as disulphides (R-S-S-R). It is present in the lower fractions boiling up to 400°F it decreases rapidly in the higher distillate cuts.

A good part of the sulphur is present in chemical forms not covered by the above group types, this is reported as "residual sulphur". It includes those higher molecular weight members or types which, because of their complex structure, or other reasons, fail to follow the reaction patterns observed by the lower molecular weight members. The residual sulphur contents in both light Arabian and Kuwait crude fractions increases in a regular manner with boiling point. The residual sulphur compounds identified in the gas oil range (400-600°F) have described as composed of thiophenic, cyclic thiols, aromatic thiols, thianthrans and thienothiophenic types [5,11].

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