8. Sulfur content of crude oils

8.1 Origin of sulfur

Sulfur in crude oil comes generally from the decomposition of organic matter, and with the passage of time and of gradual settling into strata, the sulfur segregates from crude oil in the form of hydrogen sulfide that appears in the associated gas, some portion of sulfur stays with the liquid. Another theory behind origin of sulfur compounds is the reduction of sulfates by hydrogen by bacterial action of the type desulforibrio desulfuricans:

$$4H_2 + SO_4^{=(bacteria)} \rightarrow H_2S + 2OH^- + 2H_2O$$

Hydrogen comes from the reservoir fluid and the sulfate ions are kept in the reservoir rock, as a result hydrogen sulfide is generated. The H_2S formed can react with the sulfates or rock to form sulfur that remains in composition of crude as in the case of oil from Goldsmith, Texas, USA. Moreover, under the conditions of pressure, temperature and period of formation of the reservoir H_2S can react with the hydrocarbons to give sulfur compounds (Wauquier, 1995):

$$3H_2S + SO_4 \rightarrow 4S + 2OH^- + 2H_2O$$

Sulfur compounds are among the most important non-hydrocarbon heteroatomic constituents of petroleum. There are significant amount of sulfur species found in crude oil and sulfur compounds of one type or another are present in all crude oils. Furthermore, only preferred type of sulfur exist in any particular crude oil, and this is dictated by the prevailing conditions during the formation, maturation, and even in situ alteration.

In general, the higher the density of the crude oil, the lower the API gravity of the crude and the higher the sulfur content. The total sulfur in crude oil can vary from 0.04% w/w for light crude oil to about 5% w/w for heavy crude oil and tar sand bitumen. Nevertheless, the sulfur content of crude oils which is produced from different locations varies with time, depending on the chemical composition of newly discovered fields, especially those in different geological environments (Speight, 2007).

8.2 Nature of sulfur compounds

Sulfur compounds are substances of different chemical nature, from the elemental sulfur to hydrogen sulfide and mercaptan compounds, sulfides, open-chain and cyclic disulfides, and heterocyclic derivatives of thiophene, thiophane and other more complex compounds. To date, with the exception of low molecular weight compounds, most of the sulfur compounds oils are not deciphered. Free elemental sulfur is rarely found in crude oils. The emergence of free sulfur is associated with the decomposition of more complex sulfur compounds.

The bulk of sulfur compounds found in crude oil are distributed between the heavy cuts and residues (Table 7) in the form sulfur compounds of the napthenophenanthrene or naphthenoanthracene type, or in the form of benzothiophenes, that is molecules having one or several naphthenic and aromatic rings that usually contain a single sulfur atom (Wauquier, 1995).

Table 6 *Sulfur content of selected crude oils (surface conditions) (Wauquier, 1995)*

Crude oil name	Country of origin	Weight % sulfur
Bu Attifel	Libya	0.10
Arjuna	Indonesia	0.12
Bonny light	Nigeria	0.13
Hassi Messaoud	Algeria	0.14
Ekofisk	North Sea (Norway)	0.18
Arabian light	Saudi Arabia	1.80
Kirkuk	Iraq	1.95
Kuwait	Kuwait	2.50
Cyrus	Iran	3.48
Boscan	Venezuela	5.40

Table 7 *Distribution of total sulfur in the different cuts of crude Arabian light (Wauquier, 1995)*

Cut	Light gasoline	Heavy gasoline	Kerosene	Gas oil	Residue	Crude
Temperature interval, ˚C	20-70	70-180	180-260	260-370	370+	-

Specific gravity, d_4^{15}	0.648	0.741	0.801	0.856	0.957	-
Average molecular weight	75	117	175	255	400	-
Total sulfur, weight %	0.024	0.032	0.202	1.436	3.167	1.80
Number of moles of sulfides/Total number of moles	1/1800	1/855	1/90	1/9	1/2.5	-

The sulfur compounds determined in crude oil are classified into six chemical groups.

(i) Free elemental sulfur S

Free elemental sulfur is rarely found in crude oil; however it can be present in a suspension or dissolved in the liquid. Sulfur, while crude oil is heated, partially reacts with hydrocarbons:

$$2RH+2S \rightarrow R-S-R+H_2S \qquad (X)$$

It is believed that determination of the presence of elemental sulfur in oil is a complex process and that any declaration of its presence has met with lack of confidence (Eccleston et al., 1992). The crude oil from Goldsmith, which is in Texas, is richest in elemental sulfur (1% by weight for a total sulfur content of 2.17%) (Wauquier, 1995).

(ii) Hydrogen sulfide H_2S

Hydrogen sulfide is a colorless, flammable, harmful gas that smells like rotten eggs (NPI, 2013). H_2S is found in reservoir gas and dissolved in the reservoir liquid (<50 ppm by weight). Often the appearance of H_2S in petroleum fractions is a consequence of thermal decomposition of organosulfur compounds (Ryabov, 2009). It is itself and the sulfur dioxide (SO_2), the product of H_2S combustion cause poisoning of humans, animals and plants.

The presence of H_2S in the reservoir crude determines the number of serious complications for production of oil, due to its high corrosiveness and toxicity. It causes corrosion of steel pipes and tanks, compressors, fittings and other surface equipment, particularly in the presence of carbon dioxide and water vapor in the feed, and under elevated temperatures. Therefore, the gas used as a fuel in industrial furnaces must not

contain hydrogen sulfide above the limit determined in each individual case. Furthermore, the presence of H_2S accelerates the formation of gas hydrates.

H_2S is mostly formed during processing operations such as catalytic cracking, hydrodesulphurization, thermal cracking and by thermal decomposition during distillation (Wauquier, 1995).

(iii) Thiols

Thiols or mercaptans are organosulfur compounds that contain a sulfhydryl group (SH), also known as a thiol group, that is composed of a sulfur atom and a hydrogen atom attached to a carbon atom. This molecular structure is what distinguishes thiols from other organic chemical compounds with an oxygen-to-carbon bond configuration. It is also what gives many high velocity thiols a persistent and highly unpleasant odor that is reminiscent of rotten eggs (Mayer, 2013).

The general formula of thiols is R – S – H, where R stands for an aliphatic or cyclic radical. S – H group is responsible for their acidic behavior. The level of thiols in crude oil is very low, if not zero. However, they may appear from other organosulfur compounds during refining operations, which is illustrated in Table 9. It should be noted that the content of mercaptans in crude varies from 0.1 to 15 % mass from total content of sulfur compounds (Ryabov, 2009).

Table 8 *Distribution of mercaptan sulfur among the different cuts of Arabian light crude oil (Wauquier, 1995)*

Nature of cut (temperature interval, ˚C)	Mercaptan sulfur, %	Total sulfur, %	% mercaptan sulfur / total sulfur
Crude petroleum	0,0110	1,8	0,6
Butane	0,0228	0,0228	100
Light gasoline (20-70˚C)	0,0196	0,0240	82
Heavy gasoline (70-150˚C)	0,0162	0,026	62
Naphtha (150-190˚C)	0,0084	0,059	14
Kerosene (190-250˚C)	0,0015	0,17	0,9
Gas oil (250-370˚C)	0,0010	1,40	<0,1
Residue (370 $^{+}$˚C)	0	3,17	0

Table 9 *Mercaptans identified in crude oils (Wauquier, 1995)*

Name	Chemical formula	Boiling point, ℃	Cut
Methanethiol	CH_4S	6	Butane Gasoline
Ethanethiol	C_2H_6S	34	Gasoline
2 methylpropanethiol	$C_4H_{10}S$	85	Gasoline
2 methylheptanethiol	$C_8H_{18}S$	186	Kerosene
Cyclohexanethiol	$C_6H_{12}S$	159	Gasoline

(iv) Sulfides

The sulfides are organosulfur compounds which can have a linear or ring structure. They are chemically neutral. The boiling points of sulfides are higher than of mercaptans for molecules of equal carbon number. Examples of sulfides identified in selected crude oils are shown in Table 10. They create the bulk of sulfur containing hydrocarbons in the middle distillates (kerosene and gas oil), where their content is equal to 50-80% of total sulfur compounds (Ryabov, 2009).

Table 10 *Sulfides identified in the crude oils (Wauquier, 1995)*

Name	Chemical formula	Boiling point, ℃	Cut
3 Thiapentane	$C_4H_{10}S$	92	Gasoline
2 Methyl – 3 thiapentane	$C_5H_{12}S$	108	Gasoline
Thiacyclohexane	$C_5H_{10}S$	141,8	Gasoline
2 Methylthiacyclo-pentane	$C_5H_{10}S$	133	Gasoline
Thiaindane	$C_7H_{12}S$	235,6	Kerosene
Thiabicyclooctane	$C_7H_{12}S$	194,5	Kerosene and gas oil

(v) Disulfides

The disulfides (general formula: R – S – S – R') are found in small quantities in petroleum fractions with a boiling point up to 300˚C. They account for 7-15% of the total sulfur (Ryabov, 2009).

The disulfides are complex chemical compounds which are difficult to separate; as a result, few have been identified:

Dimethyl disulfide (2,3 dithiobutane)

$CH_3 – S – S – CH_3$

Diethyl disulfide (2,3 dithiohexane)

$CH_3 – CH_3 – S – S – CH_2 – CH_3$

(vi) Thiophene and derivatives

Thiophene and its derivatives are neutral cyclic and temperature resistant compounds with five-membered ring. They do not dissolve in water, and their chemical properties are similar to aromatic hydrocarbons.

The first determination of thiophene and its derivatives was in 1899, and it was believed that they came from the degradation of sulfides during refining operations. That was until 1953, the year when the methyl-thiophenes were identified in kerosene from Agha Jari crude oil, Iran. The existence of those sulfur compounds was no longer doubted after the identification of benzothiophenes and their derivatives (Table 11).

Table 11 *Thiophene derivatives identified in crude oils (Wauquier, 1995)*

Name	Chemical formula	Boiling point, ℃	Cut
Thiophene	C_4H_4S	84	Gasoline
Dimethylthiophene	C_6H_8S	141.6	Gasoline and Kerosene
Benzothiophene	C_8H_6S	219.9	Kerosene
Dibenzothiophene	$C_{12}H_8S$	300	Gas oil