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Background

List of Abbreviations and Nomenclature

4,6-DMDBT	4,6-Dimethyldibenzothiophene
4-MDBT	4-Methyldibenzothiophene
API	American Petroleum Institute
BT	Benzothiophene
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
Cu	Copper
DBT	Dibenzothiophene
EEB	European Environmental Bureau
FCC	Fluid Catalytic Cracking
FSU	Former Soviet Union
HCR	Hydrocracking
HDS	Hydrodesulfurization
ICCT	International Council on Clean Transportation
IEA	International Energy Agency
LPG	Liquid Petroleum Gas
Ni	Nickel
NO _x	Nitrogen Oxides

NSO	Nitrogen, Sulfur and Oxygen
OPEC	Organization of the Petroleum Exporting Countries
PAHs	Polyaromatic Hydrocarbons
PASH	Polycyclic Aromatic Sulfur Heterocycles
Ph	Phytane
PM	Particulate Matters
ppm	Parts Per Million
Pr	Pristane
SO _x	Sulfur Oxides
Th	Thiophene
TLV	Threshold Limit Value
UE	Union European
ULS	Ultra-Low Sulfur
USA	United States of America
US-EPA	United States Environmental Protection Agency
V	Vanadium
WTI	West Texas Intermediate

1.1 Petroleum

Nowadays, although the percentage of energy obtained from fossil fuels has decreased, over 83% of the world's energy is still from fossil fuels, approximately half of which comes from crude oil (OPEC, 2013). Crude oil or petroleum (Black Gold) was formed under the surface of the earth millions of years ago. It is the most important renewable energy source. The largest growth in demand is from developing countries, but the largest consumers of oil are industrial nations. The OPEC has forecasted the demand for crude oil for a long-term period from 2010 to 2035, with an increasing capacity of 20 Mb/d, reaching 107.3 Mb/d by 2035 (Duissenov, 2013). It is estimated that the world consumes about 95 million barrels/per day (i.e. 5.54 trillion barrels/day) in many applications: industry, heating, transportation, generating electricity, and production of chemical reagents that can be used in making synthetics, polymers, plastics, pharmaceuticals, solvents, dyes, synthetic detergents and fabrics, fertilizers, pesticides, lubricants, waxes, tires, tars and asphalts, and many other products (Varjani, 2017). In a typical barrel, approximately 84% of the hydrocarbons present in petroleum are converted into energy-rich fuels (i.e. petroleum-based fuels); including gasoline, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas. Constituents of crude oil are resulted from aerobic and anaerobic enzymatic degradation of organic matter under suitable conditions of temperature and pressure. Crude oils vary widely in appearance

and viscosity from field to field. They range in color, odor, and in the properties they contain according to their origin and geographical place. Although all crude oils are essentially hydrocarbons that occur in the sedimentary rock in the forms of natural gas, liquid, semisolid (i.e. bitumen) or solid (i.e. wax or asphaltene), they differ in properties and in molecular structure (Berger and Anderson, 1981). It has been reported that the largest estimated crude oil reserves are in Canada, Iran, and Kazakhstan and approximately 56% of the world's oil reserves are in the Middle East. Thus, according to the regional basis, the Middle East accounts for nearly 48% of the world's reserves. Central and South America are the second with approximately 20%, with Brazil and Venezuela leading, and North America is the third with approximately 13%. Table 1.1 summarizes the world wide petroleum reserves as reported by Duissenov in 2013. However, there is a depletion of the high quality low sulfur content light crude oil coming with the increment of the production and use of high sulfur content heavy crude oil (Montiel *et al.*, 2009; Srivastava, 2012; Alves *et al.*, 2015). In the near future, with a harsh worldwide increase in energy demand, the petroleum industry will have to face the fact that sour crude oil and natural gas with high sulfur content is the only energy source of choice. For example, the sulfur content of crude oil input to refineries in USA was 0.88% in 1985, while it reached to 1.44% by 2013 (EIA, 2013).

The word of petroleum is derived from the Latin words “*petra*” and “*elaion*” (*petraoleum*) which mean rock and oil, respectively (Varjani, 2017). It is formed when large quantities of dead organisms, usually zooplankton and algae, are buried underneath sedimentary rock and subjected to both intense heat and pressure. It is a sticky, thick, flammable, yellow to black viscous mixture of gas, liquid, and solid hydrocarbons (Vieira *et al.*, 2007). It is also believed to be formed from the decomposition of animal and plants, where heat and geological pressure transform this organic matter into oil and gas during the geologic periods. Crude oil can exist either deep down in the earth's surface (onshore) or deep below the ocean beds (offshore).

Crude oils are roughly classified into three groups according to the nature of the hydrocarbons they contain: Paraffin–Base Crude Oils, Asphaltic–Base Crude Oils, and Mixed–Base Crude Oils (Varjani, 2014).

Crude oils are liquid, but may contain gaseous or solid compounds or both in solution. Crude oil varies considerably in its physical properties; the majority of crude oils are dark in color, but there are exceptions. There are also differences in odor. Many oils, such as those of Iran, Iraq, and Arabia have a strong odor of hydrogen sulfide and other sulfur compounds. There are, however, several kinds of crude oil which contain little sulfur and have unpleasant odor. This variation in properties is due to the differences in

Table 1.1 The Estimated Proven Reserve Holders as of January 2013 (Duissenov, 2013).

Country	Proven reserves (billions of barrels)	Share of total
Venezuela	297.6	18.2%
Saudi Arabia	265.4	16.2%
Canada	173.1	10.6%
Iran	154.6	9.4%
Iraq	141.4	8.6%
Kuwait	101.5	6.2%
UAE	97.8	6.0%
Russia	80.0	5.0%
Libya	48.0	2.9%
Nigeria	37.2	2.3%
Kazakhstan	30.0	1.8%
China	25.6	1.6%
Qatar	25.4	1.6%
United States	20.7	1.3%
Brazil	13.2	0.8%
Algeria	12.2	0.7%
Angola	10.5	0.6%
Mexico	10.3	0.6%
Ecuador	8.2	0.5%
Azerbaijan	7.0	0.4%
Oman	5.5	0.3%
India	5.48	0.3%
Norway	5.37	0.3%
World total	1,637.9	100
Total OPEC	1,204.7	73.6

composition and these differences greatly affect the methods of refining and the products obtained from it (El-Gendy and Speight, 2016).

A petroleum reservoir is an underground reservoir that contains hydrocarbons which can be recovered through a producing well as a reservoir fluid. In the reservoir, these fluids are usually found in contact with water

in a porous media such as sandstone and sometimes limestone. Under natural conditions, the fluids are lighter than water; they always stay above the water level and migrate upward through the porous rocks until they are blocked by nonporous rock such as shale or dense limestone. Where petroleum deposits came to be trapped can be caused by geologic features such as folding, faulting, and erosion of the Earth's crust. In most oil fields, oil and natural gas occur together, gas being the top layer on top of crude oil under which water is found.

The oil industry classifies “crude” by the location of its origin and by its relative weight or viscosity (“light”, “intermediate”, or “heavy”). Light oils can contain up to 97% hydrocarbons, while heavier oils and bitumens might contain only 50% hydrocarbons and larger quantities of other elements. The sulfur content and the American Petroleum Institute (API) gravity are the two properties that determine the quality and value of the crude oil. The API is a trade association for businesses in the oil and natural gas industries. API gravity is a measure of the density of petroleum liquid compared to water. The petroleum can be classified as light (API > 31.1), medium (API 22.3–31.1), heavy (API < 22.3), and extra heavy (API < 10.0). But, in general, if the API gravity is greater than 10, it is considered “light,” and floats on top of water. While if the API gravity is less than 10, it can be considered “heavy,” and sinks in water (El-Gendy and Speight, 2016).

In most of the international standards, the sulfur content is expressed in ppmw S or mgS/ kg (Al-Degs *et al.*, 2016). The relative content of sulfur in natural oil deposits also results in referring to oil as “sweet”, which means it contains relatively little sulfur (<0.5% S), or as “sour”, which means it contains substantial amounts of sulfur (>0.5% S) (El-Gendy and Speight, 2016). Sweet oil is usually much more valuable than sour because it does not require as much refining and is less harmful to the environment. Light oils are preferred because they have a higher yield of hydrocarbons. Heavier oils have greater concentrations of metals and sulfur and require more refining. Petroleum geochemists are using aromatic sulfur compounds as a maturity parameter. The immature oils are characterized by a relatively high abundance of thermally unstable non-thiophenic sulfur compounds, while mature oils are marked by a relatively high concentration of the more stable benzo- and dibenzo-thiophenes (Wang and Fingas, 1995). Table 1.2 summarizes the classification of crude oil according to the sulfur content and API gravity (Duissenov, 2013). The major locations for sweet crude are the Appalachian Basin in Eastern North America, Western Texas, the Bakken Formation of North Dakota and Saskatchewan, the North Sea of Europe, North Africa, Australia, and the Far East including Indonesia.

Table 1.2 Crude oil classifications according to S-content and API-gravity (Duissenov, 2013).

Crude oil class	API-gravity	Sulfur content (wt.%)
Ultra-light	>50	<0.1
Light and sweet	35–50	<0.5
Light and medium sour	35–50	0.5–1
Light and sour	35–50	>1
Medium and sweet	26–35	<0.5
Medium and medium sour	26–35	0.5–1
Medium and sour	26–35	>1
Heavy and sweet	10–26	<0.5
Heavy and medium sour	10–26	0.5–1
Heavy and sour	10–26	>1

While those for sour ones are North America (Alberta, Canada, the United States’ portion of the Gulf of Mexico, and Mexico), South America (Venezuela, Colombia, and Ecuador), and the Middle East (Saudi Arabia, Iraq, Kuwait, Iran, Syria, and Egypt) (Duissenov, 2013).

Oil is drilled all over the world. However, there are three primary sources of crude oil that set reference points for ranking and pricing other oil supplies:

Brent Crude is a mixture that comes from 15 different oil fields between Scotland and Norway in the North Sea. These fields supply oil to most of Europe.

West Texas Intermediate (WTI) is a lighter oil that is produced mostly in the U.S. state of Texas. It is “sweet” and “light” and considered very high quality. WTI supplies much of North America with oil.

Dubai crude, also known as Fateh or Dubai-Oman crude, is a light, sour oil that is produced in Dubai, part of the United Arab Emirates. The nearby country of Oman has recently begun producing oil. Dubai and Oman crudes are used as a reference point for pricing Persian Gulf oils that are mostly exported to Asia.

The OPEC Reference Basket is another important oil source. OPEC is the Organization of Petroleum Exporting Countries. The OPEC Reference Basket is the average price of petroleum from OPEC’s twelve member countries: Algeria, Angola, Ecuador, Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, the United Arab Emirates, and Venezuela.

1.2 Petroleum Composition

The chemical composition of crude oils from different producing regions, and even from within a particular formation, can vary tremendously. That depends on the location of the oil field, its age, and the depth of the oil well (Varjani, 2017). Crude oil is a complex mixture of several hundred chemical compounds, mainly hydrocarbons (mostly alkanes) of various lengths. The approximate length range is C_5H_{12} to $C_{18}H_{38}$. Any shorter hydrocarbons are considered natural gas or natural gas liquids, while long-chain hydrocarbons are more viscous, and the longest chains are paraffin wax. Generally, petroleum consists of four main fractions; saturates, aromatics, resins and asphaltenes (SARA) (Varjani, 2014). The composition percentage within the petroleum is dependent on its type. However, they are typically present in petroleum at the following percentages: paraffins (15% to 60%), naphthenes (30% to 60%), aromatics (3% to 30%), with asphaltics making up the remainder. But, in light oils, asphaltenes and resins constitute 1 to 5%. While in heavy oils, they may constitute up to 20% (Radwan, 2008). Light and less dense petroleum is more profitable as a fuel source due to its higher percentage of hydrocarbons. Since heavy and denser petroleum with high sulfur content is expensive to refine, it increases the price of gasoline (petro), diesel oil, and other important petroleum distillates. Heavy oil is characterized with high proportions of carbon and NSO and lower hydrogen and overall low quality. The world's reserves of light petroleum (light crude oil) are severely depleted and refineries are forced to refine and process more and more heavy crude oil and bitumen (El-Gendy and Speight, 2016).

Riazi (2005) has reported that crude oil composition can be summarized as follows:

- PONA (paraffins, olefins, naphthenes, and aromatics)
- PINA (paraffins, iso-paraffins, naphthenes, and aromatics)
- PNA (paraffins, naphthenes, and aromatics)
- PIONA (paraffins, iso-paraffins, olefins, naphthenes and aromatics)
- SARA (saturates, aromatics, resins, and asphaltenes)
- Based on elemental analysis (C, H, S, N, and O)

Most of the petroleum fractions are free of olefins, thus the petroleum composition can be expressed in terms of its PINA composition only. For light oils, the paraffin and iso-paraffin contents can be combined and the petroleum composition can be expressed as PNA. But, for heavy oils which are characterized by high concentrations of aromatics, resins, and

asphaltenes, the petroleum composition is expressed as SARA. Elemental analysis is very important, as it gives an indication of the hydrogen and sulfur contents as well as the C/H ratio, which is diagnostic for the quality of petroleum and its products.

Hydrocarbons are the most abundant compounds in crude oils accounting for 50–98% of the total composition (Clarck and Brown, 1977). While carbon (80–87%) and hydrogen (10–15%) are the main elements in petroleum, sulfur (0.05–6%), nitrogen (0.1–2%), and oxygen (0.05–1.5%) are important minor constituents present as elemental sulfur or as heterocyclic constituents and functional groups (Chandra *et al.*, 2013). Compounds containing N, S, and/or O as constituents are often collectively referred to as NSO compounds. Crude oils contain widely varying concentrations of trace metals such as V, Ni, Fe, Al, Na, Ca, Cu, and U (Ni plus V, <1000 ppm w/w and Fe plus Cu, <200 ppm w/w) (El-Gendy and Speight, 2016).

There are known contaminants in petroleum, which are sulfur, vanadium, iron, and zinc. Sour crude oil needs a more expensive and longer refining process, thus higher price fuel distillates and petroleum products. The foul-smelling gas, or sewer gas, mainly comes from hydrogen sulfide, which results from the decay of organic matter. All vanadium compounds are considered toxic. The V is an oxidant; it is one of the main components of diesel fuel. It causes high temperature corrosion and contributes to the corrosion of oil transport pipelines, ships, and tanker trucks. Such corrosion would cause the petroleum to be contaminated with iron which can lead to sludge build-up in pumps, refinery exchangers, and other fuel delivery systems. Moreover, V can react with other contaminants, such as sodium and sulfur, producing vandates salts which increase the corrosion of steel. If the V concentration is >2 ppm in fuels, it would lead to severe corrosion in turbine blades and deteriorate the refractories in furnaces. Moreover, heavy metals like Ni, V, and Cu severely affect the catalytic activities of refining processes and decrease the production of valuable products. Zinc is another type of contaminant which never occurs as a natural component of oil. It generally comes from the recycling of lubricating oils and interferes with the removal of salts from petroleum. This increases the salt levels which would, consequently, increase the corrosion of refinery systems, engine parts, etc.

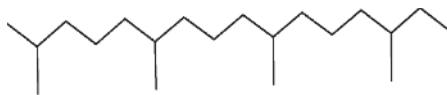
1.2.1 Petroleum Hydrocarbons

Petroleum is a complex mixture of different identifiable hydrocarbons. Hydrocarbons are organic compounds that contain only carbon and hydrogen (C_xH_y). Petroleum hydrocarbons consist of aliphatic (paraffins, olefins, and naphthenes) and aromatic compounds containing at least one benzene ring.

The alkanes, or aliphatic hydrocarbons, are a part of saturate fractions which represent the main constituent in crude oil. They consist of fully saturated normal alkanes (*n*-alkanes, also called paraffins) and branched alkanes of the general formula (C_nH_{2n+2}), with *n* ranging from 1 to usually around 40, although compounds with 60 carbons have been reported. Above C_{13} , the most important group of branched compounds is the isoprenoid hydrocarbons consisting of isoprene building blocks. Pristane (Pr, isomer of C_{19}) and phytane (Ph, isomer of C_{20}) are usually the most abundant isoprenoids and, while the C_{10} – C_{20} isoprenoids are often major petroleum constituents, extended series of isoprenoids (C_{20} – C_{40}) have been reported (Albaiges and Albrecht, 1979). The ratio of Pr to Ph is usually used to give information about the redox conditions at the time of sedimentation of the biogenic material. Moreover, this ratio can help on identification of the origin of oil in a given area (Peters *et al.*, 2005).



Pristane
2,6,10,14-Tetramethylpentadecane

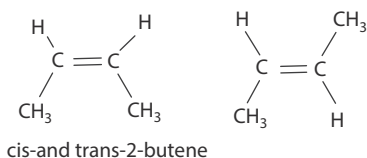


Phytane
2,6,10,14-Tetramethylhexadecane

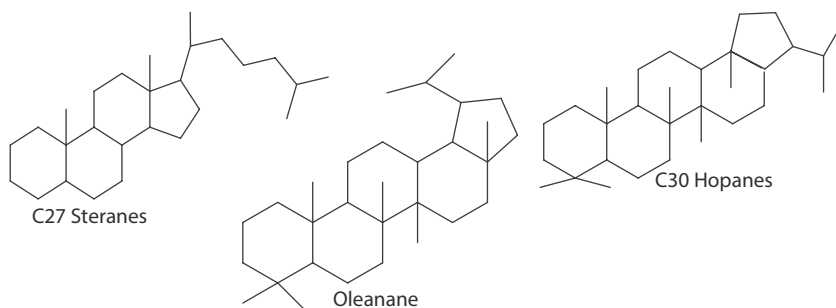
For fuel purposes only, the alkanes from the following groups will be used: pentane and octane will be refined into gasoline, hexadecane and nonane will be refined into kerosene or diesel or used as a component in the production of jet fuel, and hexadecane will be refined into fuel oil or heating oil. Alkanes with less than five carbon atoms form natural petroleum gas and will either be burned away or harvested and sold under pressure as liquid petroleum gas (LPG). Hydrocarbons longer than 10 carbon atoms in length are generally broken down through the process known as “cracking” to yield molecules with lengths of 10 atoms or less. Alkanes with a carbon number >17 are considered paraffinic waxes and are the main cause for the increase in cloud and pour points (Maldonado *et al.*, 2006). In waxy crudes, alkanes can reach up to 60%, while in low-paraffinic oils the content is recorded at about 1.2% (Duissenov, 2013).

The olefins are the unsaturated non-cyclic hydrocarbons that have at least one double bond between the carbon-carbon atoms. The monoolefins have the general formula of C_nH_{2n} . When there are two double bonds, it is called diolefin or diene. Those hydrocarbons that have one or more double bonds between carbon atoms are called alkenes. Those with one or more triple bonds between carbon atoms are called alkynes. There are two types of isomerization in olefins: the structural isomers, which is related to the location of the double bond, and the geometric isomerism, which is related to the way the atoms are oriented in the space. The configurations are differentiated by

the prefixes; *cis*- and *trans*-. Olefins and compounds with triple bonds (e.g. *cis*- and *trans*-2-butene, butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, acetylene $\text{CH}-\text{CH}$, etc.) are not commonly found in petroleum because of their tendency to become saturated with hydrogen, but they are formed during the cracking reactions in the refining process. Olefins are valuable products in refineries as they are the precursors of polymers such as polyethylene.



Many of the cycloalkanes or saturated ring structures, also called cycloparaffins or naphthenes, have the general formula C_nH_{2n} . These hydrocarbons display almost identical properties to paraffins, but have a much higher point of combustion. The content of naphthenes in crude oil can reach to 60%. However, in naphthenic crude oils it can reach to 80% (Duissenov, 2013). Saturated multi-rings attached to each other are called polycycloparaffins or polynaphthenes and are mainly found in heavy oils. Naphthenes that consist of important minor constituents like that of the isoprenoids which have specific animal or plant precursors (e.g., steranes, diterpanes, triterpanes, hopanes) serve as important molecular markers in oil spill and geochemical studies, as they are resistant to weathering. Moreover, they are used as internal preserved standard compounds in investigation of oil weathering (Albaiges and Albrecht, 1979; Daling *et al.*, 2002; El-Gendy *et al.*, 2014).



Aromatic hydrocarbons, usually less abundant than the saturated hydrocarbons, contain one or more aromatic (benzene) rings connected as fused rings (e.g., naphthalene) or lined rings (e.g., biphenyl). Some of the common aromatics that can be found in petroleum are benzene and its derivatives and methyl-, ethyl-, propyl-, or higher alkyl groups (i.e. alkylbenzens, with general formula of $\text{C}_n\text{H}_{2n-6}$, where $n \geq 6$). Monoaromatics consist of BTEX (the collective name for the benzene, toluene, ethylbenzene

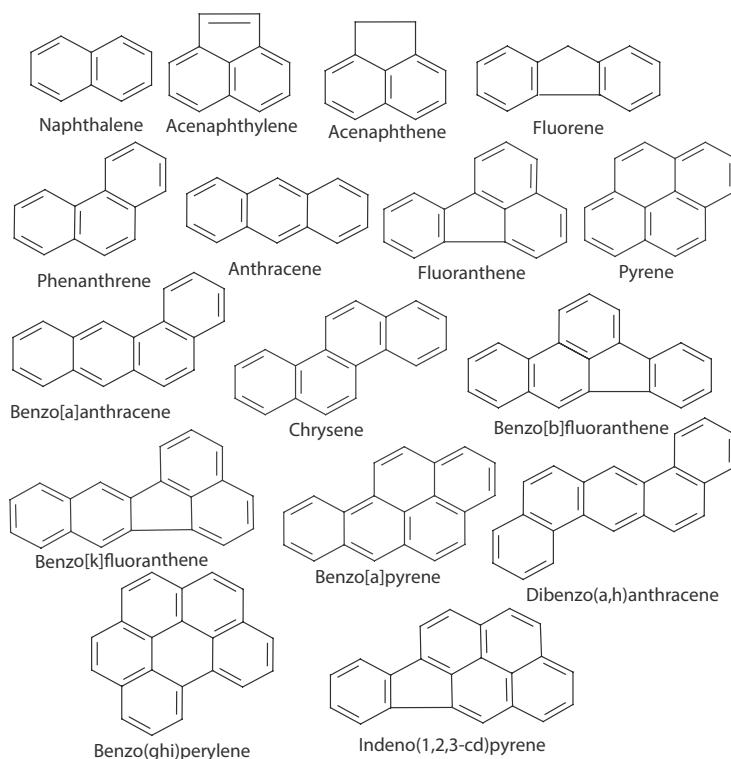


Figure 1.1 Molecular Structure of the 16-PAHs Selected by the US-EPA as Priority Pollutants.

and xylene) and mainly contribute to the octane number in gasoline. Polyaromatic hydrocarbons (PAHs) are compounds that consist of two or more aromatic rings. The United States Environmental Protection Agency (US-EPA) has selected 16 PAHs (Figure 1.1) as representative models for the toxic, mutagenic, and carcinogenic PAHs (Arun *et al.*, 2011). The PAHs up to three aromatic rings are considered low in molecular weight or light PAHs, while PAHs made up of four aromatic rings or higher are considered high in molecular weight or heavy PAHs (Wilkes *et al.*, 2016). The content of aromatics normally ranges from 15 to 20%. Usually, heavy crude oils contain more aromatics than the light ones. While in aromatic-base crude oil, aromatics content can reach to approximately 35% (Duissenov, 2013). Petroleum contains many homologous series of aromatic hydrocarbons consisting of unsubstituted or parent aromatic structures (e.g., phenanthrene) and like structures with alkyl side chains that replace hydrogen atoms. Alkyl substitution is most prevalent in 1-, 2-, and 3-ringed aromatics, although the higher polynuclear aromatic compounds (>3 rings) do contain alkylated (1–3 carbons) side groups. The polycyclic aromatics with

more than 3 rings consist mainly of pyrene, chrysene, benzantracene, benzopyrene, benzofluorene, benzofluoranthene and perylene structures. The naphthenoaromatic compounds consist of mixed structures of aromatic and saturated cyclic rings. This series increases in importance in the higher boiling fractions along with the saturated naphthenic series. The naphthenoaromatics appear related to resins, kerogen, and sterols.

Petroleum generation usually involves the formation of some naphthenoaromatic structures. The resins and asphaltene fractions differ in the proportion of aromatic carbon (Speight, 2004).

1.2.2 Petroleum Non-Hydrocarbons

Petroleum non-hydrocarbons occur in crude oils and petroleum products in small quantity, but some of them have considerable influence on product quality. They can be grouped into six classes: sulfur compounds, nitrogen compounds, oxygen compounds, porphyrins, asphaltenes, and trace metals. Nitrogen is present in all crude oils in compounds as pyridines, quinolines, benzoquinolines, acridines, pyrroles, indoles, carbazoles, and benzocarbazoles (Clarck and Brown, 1977; Hunt, 1979; Tissot and Welte, 1984).

The porphyrins are nitrogen-containing compounds derived from chlorophyll and consist of four linked pyrroles rings. Porphyrins occur as organometallic complexes of vanadium (V) and nickel (Ni); V and Ni are the most abundant metallic constituents of crude oil, sometimes reaching thousands of part per million. They are present in porphyrins complexes and other organic compounds (Yen, 1975). Oxygen compounds in crude oils (0 to 2%) are found primarily in distillation fractions above 400°C and consist of phenols, carboxylic acids, ketones, esters, lactones, and ethers. Generally, organometallic compounds are precipitated with asphaltene and resin. Sulfur compounds comprise the most important group of nonhydrocarbon constituents. In many cases, they have harmful effects and must be removed or converted to less harmful compounds during refining process.

The heteroatom contaminants must be removed before the distillate fraction is further upgraded because they poison the hydrocracking (HCR), catalytic reforming, and fluid catalytic cracking (FCC) catalysts used in subsequent downstream refining processes (Burns *et al.*, 2008).

The resins and asphaltenes contain non-hydrocarbon polar compounds, with very complex carbon structure, but the resins have lower molecular weight and are soluble in n-alkanes. The resins are amorphous solids that are completely dissolved in petroleum (Speight, 2004). However, asphaltenes are colloiddally dispersed in saturates and aromatic fractions (Speight, 2007). The resins act as peptizing agents, acting as surface-active

molecules, keeping the asphaltenes in suspension and promoting the stability of the crude oil (Speight, 2004). Petroleum asphaltenes are considered the highest molecular weight compounds in petroleum (ranging from 600 to 3×10^5 and from 1000 to 2×10^6) (Speight and Moschopedis, 1981; Kawanaka *et al.*, 1989). They belong to the group of heterocyclic compounds composed of hydrogen, nitrogen, sulfur, and oxygen and minor proportions of nickel and vanadium in porphyrines are included in its general structure (Murgich *et al.*, 1999; Tavassoli *et al.*, 2012). Asphaltenes are considered the most polar fractions in petroleum, which are soluble in benzene or toluene but not in *n*-alkanes such as pentane, hexane, or heptane (El-Gendy and Speight, 2016). Based on the effect of *n*-alkanes, they appear as solid, amorphous, or friable particles (Strausz *et al.*, 1999). Asphaltenes have a great influence upon the quality of crude oil, in such a way that they can lower its price and the price of its products if their concentration is too elevated, as many of the problems associated with recovery, separation, or processing of crude oil are related to the presence of high concentration of asphaltenes (Pineda-Flores and Mesta-Howard, 2001). Asphaltene fraction is thought to be largely responsible for adverse properties of oil; its high viscosity and its emulsion-, polymer-, and coke-forming propensities (Jacobs and Filby, 1983; Damste and De Leeuw, 1990).

Asphaltenes are dark brown to black, friable, solid components of crude oils. Their specific gravity is close to one and is highly aromatic. Asphaltene molecules carry a core of stacked, flat sheets of condensed fused aromatic rings linked at their edges by chains of aliphatic and/or naphthenic-aromatic ring systems. The condensed sheets contain NSO atoms and probably vanadium and nickel complexes (Strausz *et al.*, 1999).

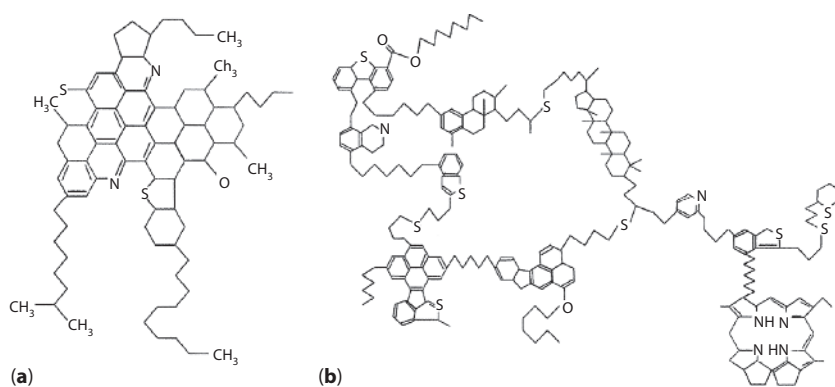


Figure 1.2 Examples of Proposed Molecular Structures of Asphaltenes. (A: Speight and Moschopedis, (1981) and B: Ancheyta *et al.*, 2009).

There are different models of asphaltene structure that coincide in showing them as a system of condensed aromatic hydrocarbons with side chains up to C_{30} , with a high proportion of heterocyclics such as benzothiophenes, dibenzothiophenes, pyrrol, pyridine, carbazole, benzocarabzole, thiophenes and sulfides, and porphyrins (Speight and Moschopedis, 1981; Murgich *et al.*, 1999; Strausz *et al.*, 1999; Pineda-Flores *et al.*, 2004; Sergun *et al.*, 2016). Figure 1.2 illustrates examples of the molecular structure of asphaltenes (Speight and Moschopedis, 1981; Ancheyta *et al.*, 2009). They are considered to be the byproduct of complex hetero-atomic aromatic macro-cyclic structures polymerized through sulfide linkages (Speight, 1970). Strausz (1988) suggested that the asphaltene molecular structure is composed of a number of polyaromatic clusters (up to 13 rings) with a few porphyrin groups bonded by heterocyclic groups and n-polymethylene bridges.

1.2.2.1 Problems Generated by Asphaltenes

It is possible to classify the problems associated to asphaltenes in five general groups: extraction, transport, processing, crude economical profit, and leaking (Pineda-Flores and Mesta-Howard, 2001).

With respect to extraction, asphaltenes have a large capability of blocking the porous spaces of the deposit, provoking a reduction of the permeability, and remarkably diminishing the crude's exit flux (Wu *et al.*, 2000).

When transporting petroleum through pipelines and metallic equipment in general, these compounds might be precipitated by the presence of ferric ions combined with acidic conditions, thus provoking the formation of a solid known as "asphaltenic mud" which deposits in conducts, blocking them and obstructing the free flow of crude. When this kind of mud develops, solvents, such as toluene and xylene, are applied in order to dissolve them. This process increases production costs and generates residues of a high degree of toxicity (Kaminski *et al.*, 2000).

As far as processing implies, asphaltenes affect petroleum refining, causing sulfur elimination to be decreased by developing a catalytic deactivation of the process through the formation of asphaltenic mud, which causes a general limitation in the maximal conversion of less-sulfured petroleum. Asphaltenes have no definite melting point and, therefore, remain in solid form, thus contributing to carbon residue (Wu *et al.*, 2000).

Regarding crude exploitation and economical profits, this is dependent on chemical composition in such a way that crude with a high content of asphaltenes (18–22%) is considered "heavy" and a low quality product. Since this represents major difficulties in its extraction and refining, economical profit notably diminishes.

Environmental petroleum leaking is the most evident way by which asphaltene and microorganisms get in touch. If we refer specifically to microorganisms, these compounds present an influence upon their distribution and activity, as they might either have a toxic effect upon microorganisms or serve them as a source of carbon and energy.

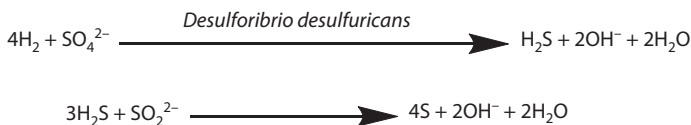
One of the gravest problems related to these compounds in the environment resides in their resistance to biodegradation by microbial metabolic activity. Due to this fact, metabolic routes involved in this process are the less known these days, although there is some evidence suggesting that some microorganisms have the potential capability of transforming asphaltene and, in the best case, eliminating them (Atlas, 1981; Guiliano *et al.*, 2000).

Nevertheless, asphaltene are useful and contribute to some of the important end used products such as paving asphalt, road oils, polymer modified asphalt, and roofing asphalt.

1.3 Sulfur Compounds

Sulfur in crude oil comes, generally, from the decomposition of organic matter and with the passage of time and gradual settling into strata, the sulfur segregates from crude oil in the form of hydrogen sulfide (H_2S) that appears in the associated gas, while some portion of sulfur stays with the liquid.

Another theory behind the origin of sulfur compounds is the reduction of sulfates by hydrogen by bacterial action of the type *Desulfuribrio desulfuricans*. Hydrogen comes from the reservoir fluid and the sulfate ions are kept in the reservoir rock. As a result, H_2S is generated which can react with the sulfates or rock to form sulfur that remains in the composition of crude. Moreover, under the conditions of pressure, temperature, and period of formation of the reservoir, H_2S can react with hydrocarbons to yield sulfur compounds (Wauquier, 1995).



Sulfur is typically the third most abundant element in petroleum (Chauhan *et al.*, 2015; Peng and Zhou, 2016). It can vary from 0.04% to 14% (wt.%) in crude oil according to its type, geographical source, and origin (Voloshchuk *et al.*, 2009; ICCT, 2011). For example, the Middle East's crude oil is richer in sulfur content than those of others, such as Indonesia (Fedorak and Kropp, 1998). However, generally, the sulfur content of petroleum falls in the range 1–4% wt. Petroleum having <1% wt.

Table 1.3 Petroleum-Sulfur Content in Different Countries All Over the World (El-Gendy and Speight, 2016).

Location	Sulfur content (wt.%)
Argentina	0.06–0.42
Australia	0–0.1
Canada	0.12–4.29
Cuba	7.03
Denmark	0.2–0.25
Egypt	0.04–4.19
Indonesia	0.01–0.66
Iran	0.25–3.23
Iraq	2.26–3.3
Italy	1.98–6.36
Kuwait	0.01–3.48
Libya	0.01–1.79
Mexico	0.9–3.48
Nigeria	0.04–0.26
Norway	0.03–0.67
Russia	0.08–1.93
Saudi Arabia	0.04–2.92
United Kingdom	0.05–1.24
USA	0.05–5
Venezuela	0.44–4.99

sulfur is referred to as low-sulfur petroleum and petroleum with >1% wt. is referred to as high-sulfur petroleum (El-Gendy and Speight, 2016). The major locations where sweet crude oil is found include the Appalachian Basin in Eastern North America, Western Texas, the Bakken Formation of North Dakota and Saskatchewan, the North Sea of Europe, North Africa, Australia, and the Far East including Indonesia, while sour crude oil is more common in the Gulf of Mexico, Mexico, South America, and Canada. Moreover, crude oil produced by OPEC Member Nations also tends to be relatively sour, with an average sulfur content of 1.77%. Table 1.3 summarizes the sulfur content in crude oils from different countries all over the world (El-Gendy and Speight, 2016). The S-content in crude oils refined in the US is known to be higher than those in the Western Europe (Song, 2003). Moreover, the S-content in Egyptian Eastern-Desert crude oils is

Table 1.4 Average Regional and Global Crude Oil Quality for 2008 (Actual) and 2030 (Projected) (The International Council of Clean Transportation ICCT, 2011)

Region	2008 (actual)		2030 (projected)	
	API gravity	Sulfur wt.%	API gravity	Sulfur wt.%
North America	31.2	1.21	28.7	1.66
Latin America	25.1	1.59	23.5	1.57
Europe	37.1	0.37	37.4	0.38
Commonwealth of Independent States	32.5	1.09	35.1	0.97
Asia-Pacific	35.4	0.16	35.7	0.16
Middle East	34.0	1.75	33.9	1.84
Africa	36.5	0.31	37.1	0.26
World Average	33.0	1.1	32.9	1.3

higher than those of the Western-Desert (El-Gendy and Speight, 2016). Table 1.4 shows the estimated crude quality, in terms of API gravity and sulfur content, in various regions of the world for 2008 (actual) and 2030 (projected) (The International Council of Clean Transportation ICCT, 2011). Most of the sulfur present in crude oil is organically bound sulfur, where more than 200 organosulfur compounds have been identified in crude oils and can be summarized in four groups: as cyclic and noncyclic compounds, such as mercaptans (R-S-H), sulfides (R-S-R'), disulfides (R-S-S-R'), sulfoxides (R-SO-R') where R and R' are aliphatic, or aromatic groups and thiophenes (thiophene, benzothiophene, dibenzothiophene and their derivatives) with hydrogen sulfide and elemental sulfur (Fedorak and Kropp, 1998; Ma, 2010; Bahuguna *et al.*, 2011). Thiophenes comprise from 50% to 95% of the sulfur compounds in crude oils and their fractions (Mohebbi and Ball, 2016). Moreover, one, two, and three sulfur atom containing compounds reach up to 74, 11, and 11% in heavy crude oils, respectively. Mercaptans content in crude varies from 0.1 to 15% mass from total content of sulfur compounds (Ryabov, 2009).

As a general rule, the higher the density of a crude oil, the lower its API and the higher its sulfur content are. Thus, the distribution of sulfur increases along with the boiling point of the distillate fraction. The sulfur content in crude oil fractions generally increases in the sequence: saturates < aromatics < resins < asphaltenes (Monticello and Finnerty, 1985). The types of organosulfur compounds that are predominant varies with

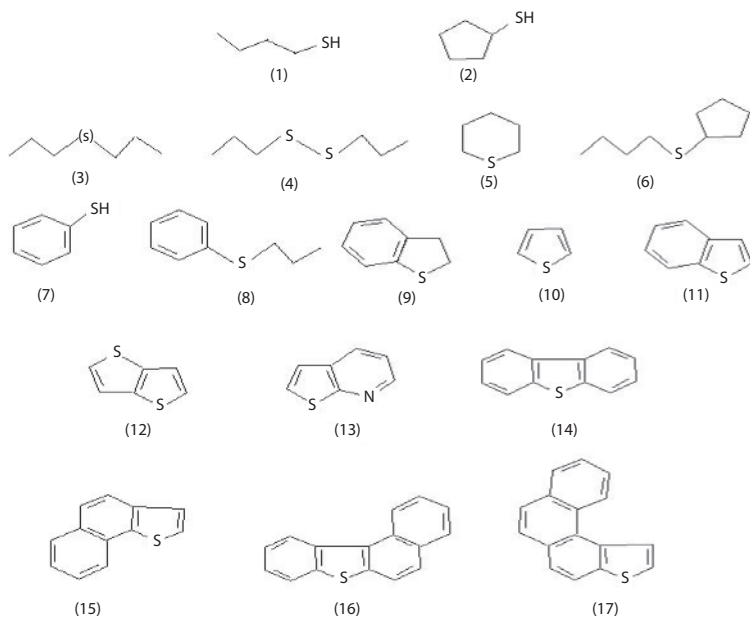


Figure 1.3 Representative Structures of the Various Types of Organosulfur Compounds Found in Petroleum. 1, alkane thiols; 2, cycloalkanes thiols; 3, dialkylsulfides; 4, polysulfides; 5, cyclic sulfides 6, alkylcycloalkylsulfides; 7, arene thiols; 8, alkyl aryl sulfides; 9, thiaindanes; 10, thiophenes 11, benzothiophenes; 12, thienothiophenes; 13, thienopyridines; 14, dibenzothiophenes 15, naphtha-thiophenes; 16, benzonaphthothiophenes; 17, phenanthrothiophenes.

the boiling range (Fedorak and Kropp, 1998). Figure 1.3 shows representative models of the various types of organosulfur compounds found in petroleum. Crude oils with higher viscosity and density usually contain high amounts of more complex sulfur compounds, although it is generally true that the sulfur content increases with the boiling point during distillation and sulfur concentration tends to increase progressively with increasing carbon number (Figure 1.4). Thus, crude fractions in the fuel oil and asphalt boiling range have higher sulfur content than those in the jet and diesel boiling range, which in turn are characterized by higher sulfur content than those in the gasoline boiling range. However, the middle distillates may actually contain more sulfur than those of the higher boiling fractions as a result of decomposition of the higher molecular weight compounds during distillation (Speight, 2000, 2006).

In fractions boiling below 150 °C, sulfur is present primarily as alkane (1) and cycloalkane (2) thiols, dialkyl (3) and alkyl cycloalkyl (6) sulfides, disulfides (4), 5- and 6- member monocyclic sulfides (5), thiophene (10), and thiophenes with one or two methyl groups. In fractions boiling

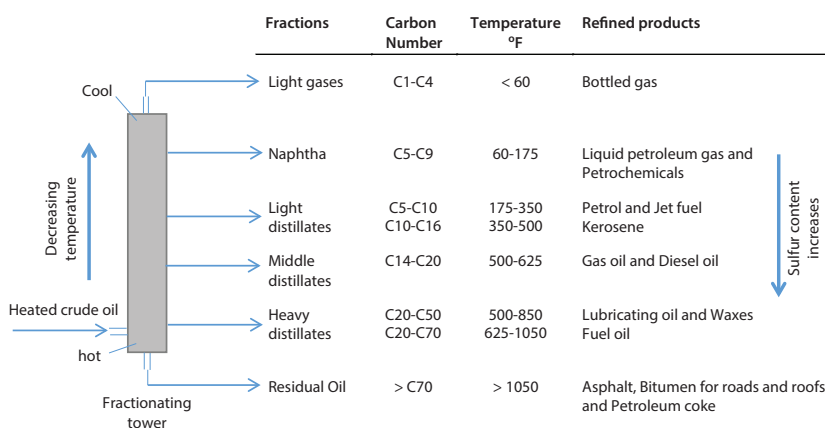


Figure 1.4 Distribution of Sulfur Content in Different Petroleum Distillates.

between 150 and 250 °C, many of these same compound types with arene thiols (7), alkyl aryl sulfides (8), polysulfides (4), and mono-, bi-, and tri-cyclic sulfides (5). As well as, thiaindanes (9), thiophenes (10) with up to four short side chains, and thiophenes condensed with one aromatic ring to form benzothiophenes (11), thienothiophenes (12), and thienopyridines (13) are typically major sulfur-containing constituents in this boiling range. The sulfur present in fractions boiling between 250 and 540 °C exists primarily in substituted thiophenes (10) and thiophene rings that are condensed to form substituted benzothiophene (11), dibenzothiophene (14), naphthothiophenes (15), benzonaphthothiophenes (16), and phenanthrothiophenes (17) (Figure 1.3). Many other complex compounds containing thiophene rings anellated with aromatic and naphthenoaromatic structures have been identified in this fraction. It was reported that >60% of the sulfur in higher boiling fractions of various crudes is present as substituted bezothiophenes. In some Middle East oils, the alkyl-substituted benzothiophenes and DBTs contribute up to 40% of the organic sulfur present (El-Gendy and Speight, 2016). Thus, benzothiophene and DBT and their alkylated derivatives are among the many condensed thiophenes that are an important form of organic sulfur in the heavier fractions of many crude oils, such as high boiling asphaltene or residue fractions. Condensed thiophenes are also the predominant form of sulfur identified in synthetic fuels derived from coal, oil shale, and tar sands. Sulfur compounds in the extremely high boiling fractions of petroleum (>540 °C) typically constitute approximately half of the total sulfur content of crude oils. While these compounds are the most difficult to analyze and identify, approximately 80% of the sulfur is estimated to be thiophenic in nature as part of larger complex molecules (Fedorak and Kropp, 1998).

1.4 Sulfur in Petroleum Major Refinery Products

Crude oil is rarely used in its raw form (with the notable exception when it is used for power generation), but must instead be processed into various products as liquefied petroleum gas (LPG), such as gasoline, diesel, solvents, kerosene, middle distillates, residual fuel oil, and asphalt. Refining is the processing of one complex mixture of hydrocarbons into a number of other complex mixtures of hydrocarbons. The safe and orderly processing of crude oil into flammable gases and liquids at high temperatures and pressures using vessels, equipment, and piping are subjected to stress and corrosion and requires considerable knowledge, control, and expertise. Refining process can be divided into three steps: separation (i.e. distillation), conversion, and treatment. It is carried out for two reasons: to separate hydrocarbons of different sizes to create different fuels and oils and to remove contaminants. Generally, a barrel of crude oil can produce approximately 42% gasoline, 22% diesel, 9% jet fuel, 5% fuel oil, 4% liquefied petroleum gases, and 18% other products (Riazi, 2005). In the distillation towers, petroleum is separated into fractions (i.e. distillates) according to weight and boiling point to light products (gas and gasolines), middle distillates (kerosene, automotive gas oil and heating gas oil), and heavy products (heavy fuel oil and bitumen). The lightest fractions, which include gasoline, rise to the top of the tower before they condense back to liquids. The heaviest fractions will settle at the bottom because they condense early. Light/sweet crude oil is generally more expensive and has great yields of higher value low boiling products such naphtha, gasoline, jet fuel, kerosene, and diesel fuel. Heavy, sour crude oil is generally less expensive and produces greater yields of lower value higher boiling products that must be converted into lower boiling products (El-Gendy and Speight, 2016). The conversion process is the the cahging of one hydrocarbon into another one. For example, the cracking process under high temperature and pressure of heavier, less valuable fractions of crude to lighter and more valuable products. Also, alkylation is another important conversion process, which is basically opposite to the cracking process. Then, finally, comes the highly technical, expensive, and most time consuming step of refining which is the treatment process. For example, optimizing the octane level in gasoline, desulfurization of diesel oil, ... etc. Figure 1.5 and Table 1.5 illustrate the type of common products obtained from crude oil distillation and cracking.

1.4.1 Gasoline

The most important refinery product is motor gasoline, a blend of hydrocarbons with boiling ranges from ambient temperatures to about 400 °F.

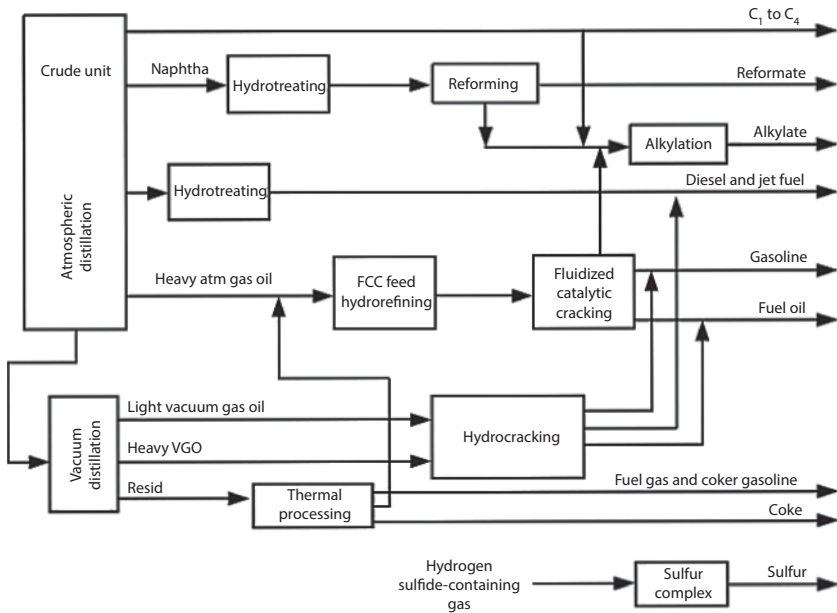


Figure 1.5 A Simplified Schematic Diagram for the Refining Process of Crude Oil (El-Gendy and Speight, 2016).

It is used as a fuel in spark-ignited internal combustion engines. The important qualities of gasoline are octane number (antiknock), volatility (starting and vapor lock), and vapor pressure (environmental control). Additives are often used to enhance performance and provide protection against oxidation and rust formation. Thiophene, benzothiophene, and their alkylated derivatives are the most common organosulfur compounds found in gasoline (Mc Farland *et al.*, 1998; Yin and Xia, 2001). The presence of sulfur in gasoline would cause corrosion in engine parts. Current gasoline desulfurization problems are dominated by the issues of sulfur removal from FCC naphtha, which contributes about 35% of gasoline pool, but over 90% of sulfur in gasoline. Deep reduction of gasoline sulfur (from 330 to 30 ppm) must be made without decreasing octane number or losing gasoline yield. The problem is complicated by high olefins contents of FCC naphtha which contribute to octane number enhancement, but can be saturated under HDS conditions (Song and Ma, 2003). Sulfur is a “poison” to FCC catalysts and many refineries have desulfurization units in front of the FCC that remove much of the sulfur from the FCC feed. However, untreated FCC products (FCC naphtha and light cycle oil) are the primary sources of sulfur in gasoline and diesel fuel. Hydrocracking has a notable advantage over FCC; the hydrogen input to the hydrocracker not only leads to

Table 1.5 Crude Oil Distillate Products (Riazi, 2005).

Distillate	Boiling range (°F)	Composition	Manufactured by	Principle uses
Gasoline	30–390	Complex mixture of materials. Contains additives to improve performance, but no polymerizable components, with very low sulfur content	Primary distillation cracking and reforming processes	Spark ignition and internal combustion engines
Kerosene	400–490	Paraffin hydrocarbons with substantial proportion of aromatics low sulfur content	Distillation, cracking	Agricultural tractors, lighting, heating, and aviation gas turbines
Diesel Oil	400–550	Saturated hydrocarbons often with high sulfur	Distillation, cracking	Diesel engines and furnace heating
Gas Oil	490–800	Saturated hydrocarbons	Distillation hydrosulfurization	Diesel fuel, heating and furnaces. Fed to cracking units

cracking reactions but also to other reactions that remove hetero-atoms, especially sulfur, from the hydrocracked streams. These “hydrotreating” reactions yield hydrocracked streams (gasoline, jet fuel, and diesel fuel) with very low sulfur content and other improved properties. Hydrocracking is more effective in converting heavy gas oils and producing low-sulfur products than either FCC or coking, but hydrocrackers are more expensive to build and operate, in large part because of their very high hydrogen consumption. Thiophene and dimethylthiophene are the main thiophenic compounds in gasoline (Wauquier, 1995).

1.4.2 Kerosene

Kerosene is a light petroleum distillate, composed of a mixture of paraffins and naphthenes with usually less than 20% aromatics. It has a flashpoint above 38 °C and a boiling range of 160 °C to 288 °C and is used for lighting, heating, solvents, and blending into diesel fuel. It has an intermediate volatility between gasoline and heavier gas oils and can be used as fuels in some diesel engines and is often used as home heating fuel. Sulfides 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), while the disulfides 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). Dimethylthiophene and benzothiophes are the main thiophenic compounds in kerosene (Wauquier, 1995).

1.4.3 Jet Fuel

Jet fuel is a middle distillate kerosene product whose critical qualities are freeze point, flashpoint, and smoke point. Commercial jet fuel has a boiling range of about 191 °C to 274 °C and military jet fuel from 55 °C to 288 °C. The main sulfur compounds in jet fuel are thiols, sulfides, and traces of thiophenes.

1.4.4 Diesel Fuel

Diesel fuel is preferred in military vehicles. Diesel has higher energy content per volume than gasoline. Because the hydrocarbons in diesel are larger, it is less volatile and, therefore, less prone to explosion. Unlike gasoline engines, diesel engines do not rely upon electrically generated sparks to ignite the fuel. Diesel is compressed to high degree, along with air, creating high temperatures within the cylinder that lead to combustion. This process makes diesel engines highly efficient, achieving up to 40% better fuel economy than gasoline powered vehicles. Diesel fuel can be

categorized according to its cetane number. No.1 diesel (super-diesel) has a cetane number of 45 and is used in high speed engines, trucks, and buses. No. 2 diesel has a 40 cetane number. Railroad diesel fuels are similar to the heavier automotive diesel fuels, but have higher boiling ranges up to 400 °C (750 °F) and a lower cetane number of 30.

The desirable qualities required for diesel fuel include controlled flash and pour points, clean burning, no deposit formation in storage tanks, and a proper diesel fuel cetane rating for good starting and combustion. In fractions used to produce diesel oil, most of the sulfur is found in BT, DBT, and their alkylated derivatives (Monticello and Finnerty, 1985). Deep reduction of diesel sulfur (from 500 to <15ppm sulfur) is dictated largely by 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in which a sulfur atom is sterically hindered by substitutions in positions 4 and 6 is the most difficult to remove by HDS; 3,6-DMDBT has been shown to be the particularly recalcitrant to HDS (Kabe *et al.*, 1997). The deep HDS problem of diesel streams is exacerbated by inhibiting effects of the co-existing problem of polyaromatics and nitrogen compounds in the feed as well as H₂S in the product (Song and Ma, 2003).

Because of the similar distillation points of diesel and sulfur contaminants, they are produced together during the refining process. Due to the strict international regulations, additional steps are taken to remove the sulfur. That makes diesel fuel cost more than gasoline.

1.4.5 Heating/Fuel Oils

Domestic heating oils have boiling ranges of about 400–700 °F. They consist of hydrocarbons of a chain length between eight and 21 carbon atoms. It is a general meaning that intermediate hydrocarbon liquid mixtures have lower volatility than that of kerosene. They contain a relatively high content of sulfur.

Heating/fuel oils are one of the “left-over” products of crude refining; they are less pure than other refined products, with a broader range of hydrocarbons. They are characterized with high flash points and are more prone to auto-ignition, producing more pollutants on combustion. However, No. 1 fuel oil is similar to kerosene and No. 2 fuel oil is very similar to No. 2 diesel fuel. Heavier grades of No. 3 and 4 are also available.

1.4.6 Bunker Oil

Bunker oil is one of the bottom products of petroleum refining. It is mainly used as marine fuel for shipping. It is a complex mixture of alkanes, alkenes with high content of aromatic hydrocarbons, and asphaltenes which leads to its high viscosity. It is characterized by high sulfur content, ranged between 1.5 to 4 wt.%, upon its combustion and it produces elevated concentrations of SO_x.

emissions. It has been reported that the SO_2 from shipping activities reached 16.2 million tonnes by 2006 and it is expected to be raised to reach about 22.7 million tonnes by 2020 (The European Environmental Bureau EEB, 2008).

1.5 Sulfur Problem

The depletion of continental crude oil deposits has forced the exploitation of deeper reservoirs containing petroleum rich in polynuclear aromatic sulfur heterocyclic (PASH) compounds and other unconventional oil reserves including heavy oil, extra heavy oil, and oil sands and bitumen, which comprise 70% of the world's total oil resources (US EIA, 2010). Also, with the rising of oil prices, the production of synthetic crude oil from unconventional resources, such as oil sands, is becoming increasingly economically viable (US EIA, 2010). Canada, Venezuela, and the US have extremely large deposits of heavy oil and oil shale. Unconventional oil reserves are characterized by large quantities of sulfur, nitrogen, nickel, and vanadium, for example, Athabasca oil sand bitumen has a sulfur content of 4.86% (Bunger *et al.*, 1979). The sulfur content in heavy crude oil varies from 0.1% to 15% (w/w) (Shang *et al.*, 2013).

Sulfur compounds are very undesirable because of their disagreeable odor, deleterious effect on color or color stability, and unfavorable influence on antiknock and oxidation characteristics. Organosulfur compounds in crude oil increase the viscosity of a large fraction making it non-amenable to the refinery process (Chauhan *et al.*, 2015). They have actual or potential corrosive nature, which would cause the corrosion of pipelines and pumping and refining equipment. The annual cost of corrosion worldwide is reported to be approximately \$3.3 trillion (Duissenov, 2013). Sulfur compounds contaminants, such as polysulfides, mercaptans, and aliphatic sulfides, can react with metal surfaces at high temperatures forming metal sulfides, organic molecules, and H_2S hydrogen sulfide. The corrosiveness of sulfur compounds in the form of uniform thinning, localized attack, or erosion-corrosion, increases with accumulating temperature, which is very dangerous, especially at high temperature and pressure since fire would occur upon sudden rupturing due to corrosion. Sulfur compounds are undesirable in refining processes as they tend to deactivate, i.e. poison the catalysts used in downstream processing and upgrading of hydrocarbons (El-Gendy and Speight, 2016). In liquid petroleum products, sulfur compounds would contribute to the formation of gummy deposits which would plug the filters of the fuel-handling systems of automobiles and other engines. Sulfur compounds in fuel oils would cause corrosion to the parts of the internal combustion engines and, consequently,

their breakdown and premature failure (Collins *et al.*, 1997). Sulfur levels in automotive fuels have an unfavorable poisoning effect on the catalytic converters in automotive engines, thus increasing the particulate, CO, CO₂, SO_x, NO_x, and other combustion related emissions, that cause smog, global warming, and water pollution (Srivastava, 2012). The presence of sulfur in lubricating oils lowers the resistance to oxidation and increases the solid deposition on engine parts (Riazi *et al.*, 1999).

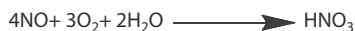
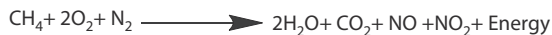
Consequently, refineries must have the capability to remove sulfur from crude oil and refinery streams to the extent needed to mitigate these unwanted effects, where corrosion by different sulfur compounds at temperatures between 260 and 540 °C is a general issue in petroleum refining and petrochemical processes. However, the higher the sulfur content of the crude, the greater the required degree of sulfur control and the higher the associated cost. Sulfur removal is also important for the new generation of engines, which are equipped with a nitrogen oxide (NO_x) storage catalyst, since sulfur in the fuel has poisoning effects on the catalyst (König *et al.*, 2001). The significant reduction of sulfur-induced corrosion and the slower acidification of engine lubricating oil would lead to lower maintenance costs and long maintenance intervals. These are also additional benefits of using ultralow sulfur diesel in diesel powered vehicles (Stanislaus *et al.*, 2010). It is believed that refining industries will spend about \$37 billion on new desulfurization equipment and an additional \$10 billion on annual operating expenses during the next decade to meet the new sulfur regulations. In addition to this opportunity in the refinery, there is also a large potential in the desulfurization of crude oil itself (Mohebbi and Ball, 2008).

Emissions of sulfur compounds (e.g. SO₂ and fine particulate matter of metal sulfates) formed during the combustion of petroleum products are the subject of environmental monitoring in all developed countries. It has been reported that approximately 73% of the produced SO₂ is from anthropogenic origin and is due to the combustion of petroleum and its derivatives (Aparicio *et al.*, 2013). As SO₂ is transported by air streams, it can be produced in one area and show its adverse impact in another remote place thousands of kilometers away (Soleimani *et al.*, 2007). These harmful emissions affect the stratospheric ozone, increasing the hole in the Earth's protective ozone layer (Denis, 2010). High levels of SO₂ cause bronchial irritation, trigger asthma, and prolonged exposure can cause cardio-pulmonary and lung cancer mortality (Mohebbi and Ball, 2008). Furthermore, sulfur compounds have unfavorable influences on antiknock and oxidation characteristics. High concentration of sulfur in fuels dramatically decreases the efficiency and lifetime of emission gas treatment systems in cars (Mužić and Sertić-Bionda, 2103).

Incomplete combustion of fossil fuels causes the emission of aromatic sulfur and nitrogen compounds and oxidation of these compounds in the atmosphere would lead to the aerosol of sulfuric and nitric acids. For example, NO_x emission would be significantly increased by 66%, corresponding to an increase in sulfur content of gasoline from 40 to 150 ppm (US EPA, 1998). NO_x and CO_2 are thought by many to be the primary causes of “chemical smog”, as well as “greenhouse gas” accumulation (Nasser, 1999). It has been reported that sulfur is the main cause of emissions of PM (Mohebbi and Ball, 2016). Stanislaus *et al.* (2010), reported that approximately 2% of sulfur in diesel fuel can be directly converted to PM emissions. PM is carcinogenic and, moreover, PM and SO_x cause lung cancer and cardiopulmonary mortality. Soot and smoke both refer to particulate matter (PM) that gets trapped in gases during combustion. The visible, dark black component of smoke is carbon that has incompletely burned and, rather than forming CO_2 , has formed solid carbon compounds known as amorphous carbon. These carbon compounds are collectively referred to as soot, which resulted from the use of the lower quality of fuel (i.e. a less refined one). Soot, in particular, contains large amounts of the mutagenic and carcinogenic PAHs. Diesel exhaust is considered the most carcinogenic of transportation fuels and accounts for approximately 25% of all smoke and soot in the atmosphere.

The health effects of sulfur oxides SO_x include irritation in the eyes, nose, and skin and can lead to acute bronchitis and severe respiratory disorders when inhaled by humans (Grossman, 2001; Bordoloi *et al.*, 2014; Martinez *et al.*, 2015; Agarwal *et al.*, 2016; Martinez *et al.*, 2017).

Moreover, upon the emissions of SO_2 and NO_2 in the atmosphere, they react with hydrogen producing weak sulfurous acid, strong sulfuric acid, and nitric acid which are the main causes of acid rain and haziness that reduce the average temperature of an affected area (Derikvand *et al.*, 2014).



Acid rain has a deleterious effect as it causes soil pollution, destroys green area, kills forests, and damages crops, leather, cars, and buildings. It also poisons lakes and rivers leading to a devastating effect on their fauna and flora and a falling in fish population. Also, the presence of high levels of sulfate in water affects human health, as it causes diarrhea and dehydration (Grossman, 2001; Ardakani *et al.*, 2010; Mohebbali and Ball, 2016; Paixao *et al.*, 2016).

H₂S present in crude oil and its low boiling distillates is one of the most corrosive sulfur compounds and would destroy paintings and buildings. Moreover, it is the main component of refinery sour waters, thus, it would cause corrosion problems in overhead systems of fractionation towers, hydrocracker and hydrotreater effluent streams, catalytic cracking units, sour water stripping units, and sulfur recovery units.

H₂S is a highly toxic gas that affects the nervous and respiratory systems causing symptoms that include headache, dizziness, and excitement. It is like cyanide in that it inhibits the cytochrome oxidase system essential for respiration (Manahan, 2003). It is reported that it may even have contributed to several mass extinctions in Earth's past (Duissenov, 2013). The personal risk arises when people are exposed to contaminated air with concentrations above the threshold limit value, T.L.V. (10 ppm). Deadly H₂S (1000–2000 ppm) can kill an operator in 10 seconds (Table 1.6). Fortunately, sulfides have a highly obnoxious smell which gives some warning of their danger.

H₂S is actually very flammable, so it could be used as a fuel if it were not for the fact that it is also deadly in relatively low concentrations. This deadly gas must be removed from petroleum in order to make it safer for use. The hydrogen sulfide can then be used to produce pure sulfur, a highly valued industrial element used in the production of fertilizer.

Light alkyl thiols, such as methanethiol, are fairly common air pollutants with odors that may be described as ultragarlic. Inhalation of even very low concentrations of the alkyl thiols in air can be very nauseating and result in headaches. Exposure to higher levels can cause increased pulse rate, cold hands and feet, and cyanosis. With extreme cases, unconsciousness, coma, and death may occur (Manahan, 2003).

Table 1.6 Toxicity of H₂S.

Low	Medium	High
Coughing	Fainting	Strangling
Burning sensation	Pallor	Rapid loss of conscious
Pain in eyes	Cramps	Loss of heart beats
Sleepiness	Breathing may stop, but may return	Loss of breathing Pupils dilated

The large-ring thiophenes and polycyclic aromatic sulfur heterocycles (PASHs) are among the most potent environmental pollutants and exhibit some mutagenic and carcinogenic activity (Murphy *et al.*, 1992; Jensen *et al.*, 2003). Observations and analyses associated with oil spills and chronic pollution have indicated that the PASHs are more resistant to microbial degradation, accumulated to a greater degree and departed more slowly than their polyaromatic hydrocarbon (PAHs) analogs (Durate *et al.*, 2001). For example, organic sulfur compounds found in crude oil usually serve as makers of oil pollution in fish and shell fish. GC/MS analysis of the extracts showed the presence of organic sulfur compounds of alkyl- (from mono- to penta-methyl) benzothiophenes, dibenzothiophene and alkyl-(from mono- to tri-methyl) dibenzothiophenes, and other organic sulfur compounds of alkyl- (from mono- to penta-methyl) naphthalenes (Ogata and Mujake, 1978 and Ogata and Fujisawa, 1983). It has been reported that DBT and its derivatives can persist for up to three years in the environment (Gundlach *et al.*, 1983).

1.6 Legislative Regulations of Sulfur Levels in Fuels

Worldwide environmental legislation has put limits for the sulfur levels in transportation fuels to decrease SO_x emissions. Consequently, refineries must have the capability to remove sulfur from crude oil and refinery streams to the extent needed to mitigate its negative impact and reach the restricted regulatory sulfur limits. Moreover, international cooperation is required to limit and control the SO_x emissions. The American Lung Association reported that low-sulfur fuel would reduce the soot amount from large trucks by approximately 90% (Riazi, 2005). Ultra-low sulfur (ULS) fuels significantly reduce total fuel cost by increasing fuel economy, since the considerable potential for reduction in greenhouse gas emissions adds further payback to health, environmental, and social benefits (Blumberg *et al.*, 2003).

Since 1979, Canada, Japan, the United States, and the European nations in particular have signed several agreements to reduce and monitor emissions of SO_2 . Most of these agreements targeted transport fuel because it was one of the important sources of SO_2 . For example, the US-EPA and other regulatory agencies worldwide have limited the amount of SO_2 released into the air and put strict regulations and limits for the sulfur content in transportation fuels; 15 and 30 ppm for diesel oil and gasoline, respectively (Agarwal *et al.*, 2016; Al-Degs *et al.*, 2016). Moreover, the sulfur content limits in the EU, set by Euro V norms, has reached 10 ppm since 2009 and 15 ppm for the US since 2006 to ultra-clean fuels <1 ppm

in the near future, approaching zero-sulfur emissions upon fuel combustion (Calzada *et al.*, 2011; Zhang *et al.*, 2011; Martinez *et al.*, 2015; Al-Degs *et al.*, 2016). In China, the sulfur content in gasoline and diesel oil is targeted to be 10 ppm by 2016 (Yang *et al.*, 2014), while in most of the developed countries the acceptable sulfur level in gasoline has been restricted to be <10 ppm (Shang *et al.*, 2013). In India, the sulfur content in gasoline has lowered to 50 ppm since 2010 in 13 selected cities, whereas the nationwide sulfur gasoline level is 150 ppm. Several other countries around the world are moving forward with lowering the maximum fuel sulfur content. This is particularly true in the Middle East, Russia, South Africa, and some countries in Latin America. Saudi Arabia and Russia have put the limitation of 10 ppm of gasoline by 2013 and 2016, respectively. South Africa has agreed to enforce 10 ppm gasoline by 2017 (OPEC, 2011). However, a much higher level (350 ppm) is permitted for transportation fuels in Jordan and some other countries (Al-Ghouti and Al-Degs, 2014).

The European Fuel Quality Directive has required the on-road and off-road diesel fuel sulfur content to be set at 10 ppm since 2011. Same maximum level of 10 ppm was legislated in Japan, Hong Kong, Australia, New Zealand, South Korea, and Taiwan. In Canada and the US, the maximum level is 15 ppm since 2010 and 2012, respectively. China planned to reduce its on-road diesel sulfur to 350 ppm in July 2012. However, at the more regional level, Beijing has a diesel sulfur limit of 10 ppm, while the cities of Shanghai, Guangzhou, Shenzhen, Dongguan, and Nanjing have required a 50 ppm maximum since May 2012. India has also set a maximum level of 50 ppm for 20 urban centers, while its national specification is 350 ppm. Other Asian countries including Indonesia, Malaysia, the Philippines, and Thailand are putting plans together to catch the wave. The majority of Latin America has sulfur limits for diesel oil above 500 ppm. However, premium diesel in Argentina was set to 10 ppm since 2011 and Chile has a set limit of 50 ppm of diesel since 2006. In Brazil, diesel specification limits the amount of sulfur down to 10 ppm by 2013, Ecuador and Mexico are in their way to follow the sulfur level limitations. But, in Africa, the average sulfur content is in the range of 2,000 to 3,000 ppm for on-road diesel, and is much higher for off-road, while South Africa planned to reach to 10 ppm fuels by 2017. Briefly, with the exception of Africa, all regions worldwide, are projected to reach an average on-road sulfur content of <20 ppm by 2035 (OPEC, 2011). The projected sulfur content in gasoline and diesel oil for 2012–2035 are shown in Tables 1.7 and 1.8 respectively.

In developed countries, regulations have been set for heating oil, jet kerosene, and fuel oil. The EU has reduced the sulfur content distillate-based heating oil from 2,000 ppm to 1,000 ppm since 2008. Germany provides

Table 1.7 Expected Regional Gasoline Sulfur Content (OPEC, 2013).

Location	S-content in gasoline ppm					
	2012	2015	2020	2025	2030	2035
US and Canada	30	30	10	10	10	10
Latin America	520	255	130	45	30	20
Europe	13	10	10	10	10	10
Middle East	605	235	75	25	16	10
FSU	315	115	35	20	12	10
Africa	795	493	245	165	95	65
Asia-Pacific	205	130	65	35	20	15

Table 1.8 Expected Regional On-Road Diesel Sulfur Content (OPEC, 2013).

Location	S-content in on-road diesel ppm					
	2012	2015	2020	2025	2030	2035
US and Canada	15	15	15	10	10	10
Latin America	1085	440	185	40	35	20
Europe	13	10	10	10	10	10
Middle East	1725	415	155	70	20	10
FSU	440	175	60	15	10	10
Africa	3810	2035	930	420	175	95
Asia-Pacific	400	200	100	45	25	15

tax incentives for 50 ppm heating oil to enable the use of cleaner and more efficient fuel burners. Parts of North America plan to reduce sulfur levels in heating oil to 15 ppm before 2020 (Duissenov, 2013).

In industrialized regions in Europe, reductions in the sulfur content of jet fuel is aimed to reach 350 ppm by 2020, followed by other countries by 2025. Industrialized regions are also assumed to reach 50 ppm by 2025. However, the current jet fuel specifications still allow for sulfur content as high as 3,000 ppm, but there is jet fuel with 1,000 ppm sulfur content (OPEC, 2011). Marine bunker fuels are also subject to regulation. As of January 2012, the global sulfur cap was lowered from 4.5 wt.% to 3.5 wt.% and will be further lowered to 0.5 wt.% (5,000 ppm) as of January 2020. In September 2012, the European Parliament approved final legislation requiring all ships in EU waters to switch to 0.5% wt sulfur fuel or use corresponding technology allowing ships to reach the required emissions reduction by 2020 (OPEC, 2011; Tang, 2013).

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