

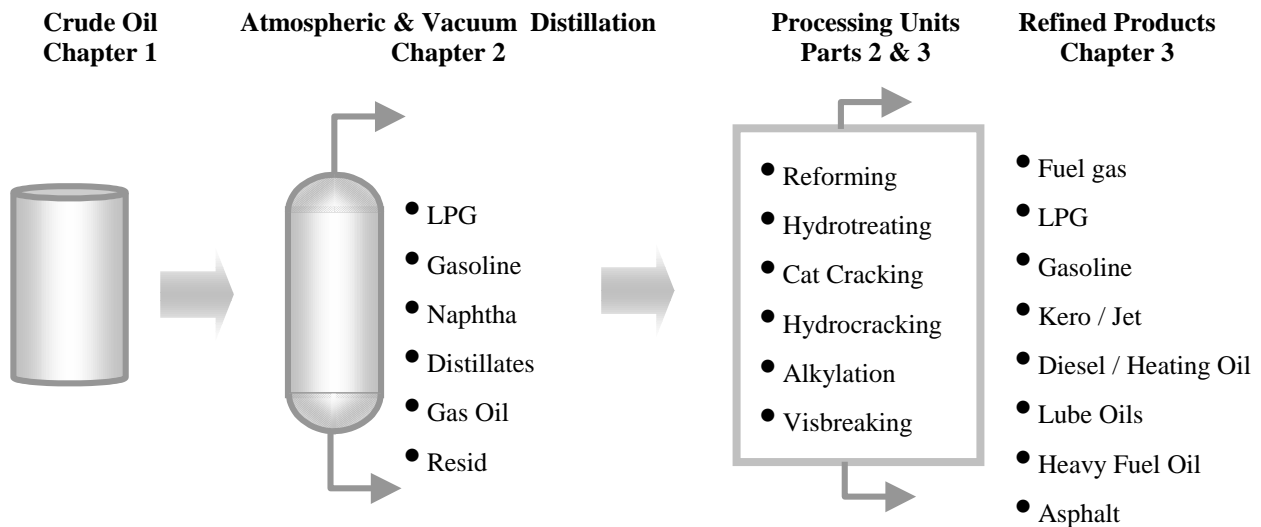
CHAPTER 1 THE NATURE OF CRUDE PETROLEUM

About This Chapter

For most of history crude oil was a nuisance. It had no widespread commercial application, although evidence for water proofing and cement can be found more than several thousands years B.C. The use of petroleum products for illumination and incendiary devices can be traced back almost one thousand years B.C. But in the middle of the 1800s, when visionaries first recognized a broad market, the products were illuminating kerosene, steam engine lubricants, and harness leather treatment with the rest of the crude discarded as waste. Today the primary products are transportation fuels. The whole industry is founded on providing marketable products from crude oil fractions and the development of technologies to produce those products.

This chapter introduces crude oil as a mixture of compounds. The characteristics of these compounds will provide insights to processing.

The next chapter will discuss petroleum in terms of the fractions from the atmospheric and vacuum units. The atmospheric and vacuum units are the first units in the process and the fractions from these units lead directly into further processing units. The third and final chapter in this part will describe refined products and an overview of specifications.



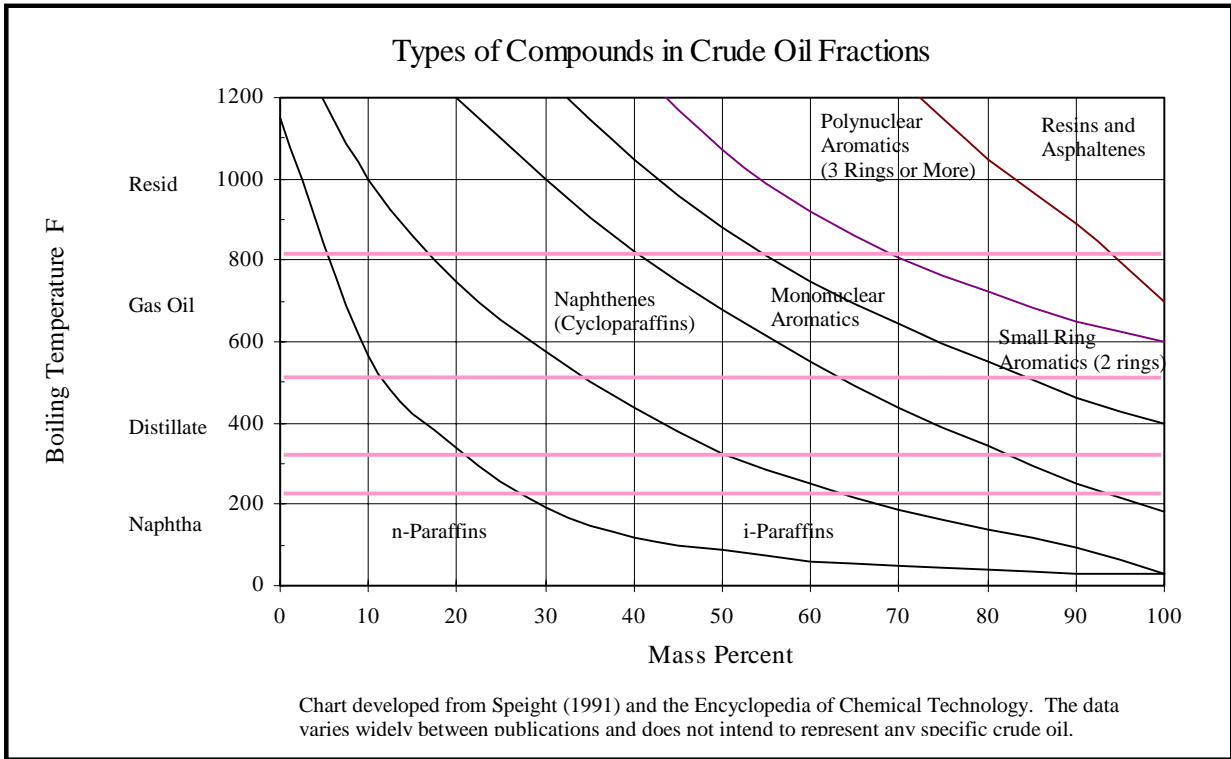
The Nature of Petroleum

Crude oil is a mixture of hydrocarbons with between 100,000 to 1,000,000 different molecules contributing to a boiling range well over 1,000^o F. At the lower end are the gaseous products, methane and ethane and various inorganic gases such as hydrogen sulfide and carbon dioxide.

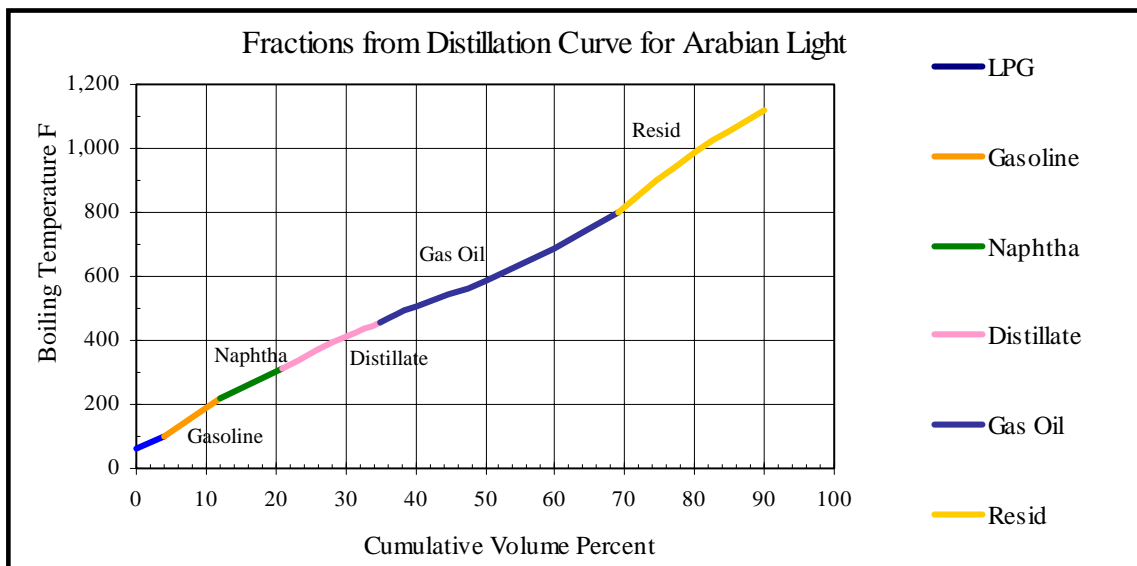
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At the upper end, the material becomes non-volatile at about 1100°F, distillation temperature, with the remainder being resins and asphaltenes, which are complex hydrocarbon multi-ring aromatic structures imbedded with varying degrees of sulfur, nitrogen, oxygen, and heavy metals such as vanadium and nickel.

The following chart illustrates the types of compounds in crude oil. It has been developed as a function of the products from the atmospheric and vacuum towers, a typical reference point.



For an analogous contrast, the distillation curve is also provided for the products from the atmospheric and vacuum towers.



Classification of Petroleum and Petroleum Compounds

There are many classifications for crude oil. Presented here will be a classification system simple but sufficient to understand the issues associated with manufacturing refined products. If one researches into the issues of catalysis or advanced resid conversion processes, then more sophisticated and complex models are required and described in the literature. The classification will group petroleum components into the following classes.

- Normal paraffins
- Iso-paraffins
- Olefins
- Cycloparaffins (naphthenes)
- Mononuclear aromatics
- Polynuclear aromatics (PNA)
- Resins
- Asphaltenes
- Heteroatom compounds

Normal Paraffins are predominant in the low boiling point ranges. Paraffins are not generally used in gasoline because of their low octane number, which is a measure of the tendency to auto-ignite and knock. However, they are easily isomerized in the Reformer Unit to improve octane. Paraffins with carbon numbers of eleven and higher are used in kerosene because they produce less smoke and used in diesel because they autoignite (diesel). Paraffin wax consists of carbon numbers twenty and higher.

Iso-Paraffins are the generic industry term for all branched chain paraffins. Iso-paraffin structures possess high anti-knock characteristics and provide high octane numbers for gasoline.

Olefins contain at least one double bond with no aromatic or cycloparaffinic rings. Crude oil contains none or only small amounts of olefins with not enough to affect processing.

Cycloparaffins (naphthenes) are known as in the industry as naphthenes and should not be confused with the compound naphthalene, a binuclear aromatic. They are also sometimes called alicyclics as opposed to aliphatics compounds without rings. Common naphthenes are cyclopentane, cyclohexane and their homologues created by the addition of side chains to the saturated ring compound. Naphthenes in the gasoline range are desirable because they can be converted to aromatics by dehydrogenation. Naphthenes are also desirable for lube stocks due to satisfactory viscosity, pour point, and oxidation and thermal stability.

Cyclopentane



Methylcyclopentane



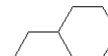
Cyclohexane



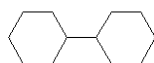
Methylcyclohexane



Ethylcyclohexane



Bicyclohexane

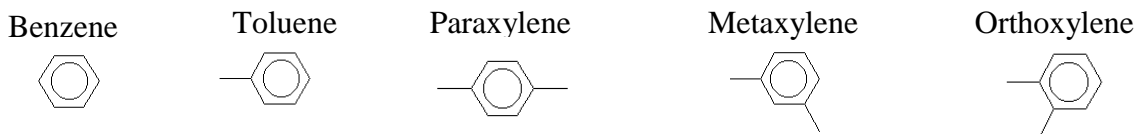


Benzocyclohexane (tetralin)



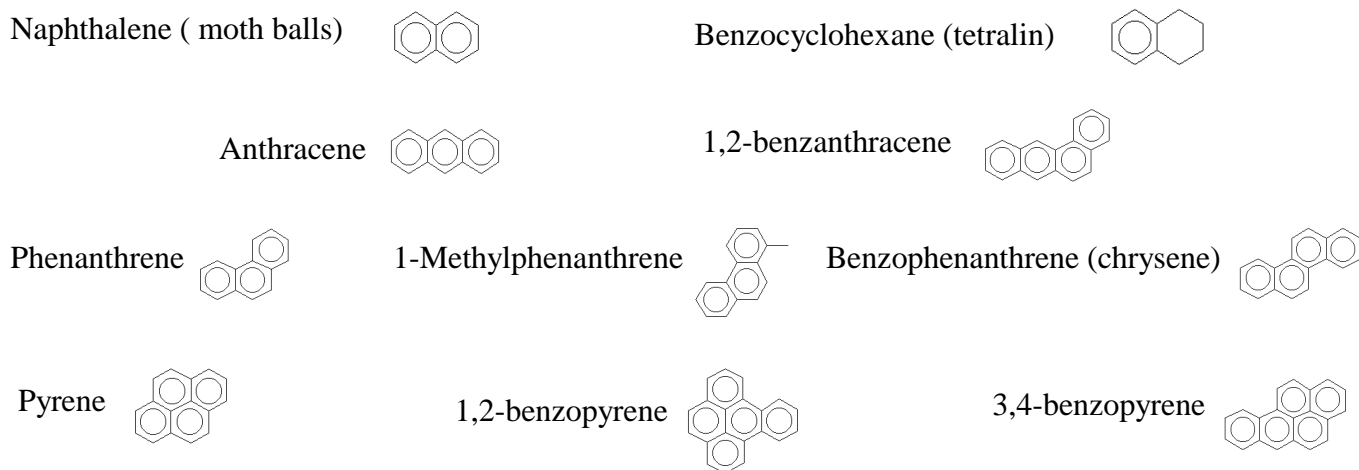
Mononuclear Aromatics have at least one benzene ring in the molecule. Their name is derived from the pronounced odor of many organic compounds. The three basic materials for most intermediate derivatives are benzene, toluene, and the xylenes (commonly called BTX). Toluene and xylene are desirable for gasoline

because they have high octane numbers. However, they are being reduced in reformulated fuels for environmental reasons. Benzene, because of its value for chemical feedstock, was never a major constituent and is now limited by environmental concerns.



Polynuclear Aromatics (PNA) have two or more aromatic rings. Aromatics with only two rings are often called “small ring aromatics” (SRA) or just “aromatics”. The term polynuclear aromatic (PNA) is usually reserved for aromatics with three or more rings. While both small ring and multiple ring structures contain sulfur, multiple rings also contain nitrogen, oxygen, vanadium and nickel in their structures. Molecular weights average between 150 and 500. Polynuclear aromatics (PNA) have low hydrogen to carbon ratios with hydrogen percent by weight between 9% and 12%. Thermally stability is one characteristic important during coking.

Aromatic rings may be classified into types: • condensed such as naphthalene, • linked by bond such as biphenyl, or • linked by non-aromatics such as phenylmethane. • Other designations have also been employed such as “naphthenoaromatics” used for benzocyclohexane (tetralin).



Resins are thought to be lower molecular weight analogs of asphaltenes. Molecular weights average between 500 and 1,500 with hydrogen percent by weight between 7% and 10%. One model, as further described below with the section on asphaltenes, suggests that a resin molecule is composed of one polynuclear aromatic (PNA) surrounded by side chains of saturated paraffins, partially saturates, and small ring aromatics. Each polynuclear aromatic may have three to six rings containing sulfur, nitrogen, oxygen, vanadium and nickel. The side chains do not contain appreciable heteroatoms. As in asphaltenes, volatile liquids are formed from the side chains if they are cracked from the polynuclear aromatics.

Asphaltenes are complex. They are generally believed to have high molecular weights ranging from 500 to 4,500 with values of 100,000 being reported. Hydrogen percent by weight is between 5% and 8% indicating the highest aromaticity of any other crude oil fraction. Additionally asphaltenes have greatest number of heteroatom (atoms other than carbon and hydrogen). Although asphaltenes are thought to be higher molecular weight analogs of resins, basic properties of asphaltenes, such as molecular weight, are difficult to

experimentally measure with current techniques. This is because of the lack of volatility, the affinity to adsorb on materials, and the tendency in solvents to self-associate and form colloidal dispersions rather than to form solutions in solvents.

Even more taxing, asphaltenes are difficult to structurally visualize. One crude fraction may be composed of 100,000 different molecular structures with variations in the heteroatoms contributing to the diversity. To understand the structure of asphaltenes, one must consider the number of polynuclear aromatics, the ring size distribution of each PNA, and the arrangement of heteroatoms (sulfur, nitrogen, oxygen, vanadium and nickel). Although solubility and bonding are of great research interest they are out of the scope of this overview.

A long-standing model for asphaltenes is that of a complex molecular "chicken wire" polymeric type structure composed of sheets of condensed polynuclear aromatics with twenty or more rings. Paraffinic and naphthenic chains link the sheets. Heteroatoms are distributed throughout. Reported molecular weights of up to 100,000 supported this hypothesis.

One recent asphaltene model portrays polynuclear aromatics as cores, stacked in short columns, with two or more cores per stack and several stacks per molecule. Each polynuclear aromatic core may have three to six rings and contain sulfur, nitrogen, oxygen, vanadium and nickel distributed in their structure. Surrounding the cores are pendant fragments which are side chains of saturates, partially saturates, and small ring aromatics. Noteworthy is that pendants, unlike the cores, do not contain appreciable heteroatoms. If the pendants are cracked off the cores, the pendants form volatile liquids. This model is useful in describing coking and hydroprocessing operations [Wiehe (1998) and Speight (1999)].

One dramatic characteristic of asphaltenes is their tendency to precipitate in the presence of propane and butanes (such as during crude blending or production operations) or after removal of resins and small ring aromatics (such as during thermal processing), leading to plugging and coking. Precipitation is related to the decrease in solubility of the asphaltene, already the least soluble fraction in petroleum due to high molecular weight and high aromaticity.

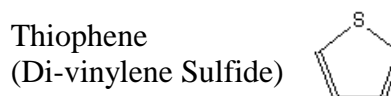
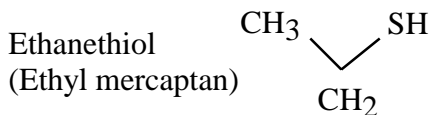
Asphaltenes and resins are a necessary component of crudes used to make asphalts. Asphaltenes must be present in a heavy bottom fraction to make petroleum grade asphalts. However, the presence of resins and asphaltenes complicates the choice of conversion options for vacuum resid. Although hydroprocessing reduces the formation of large polynuclear aromatics (three rings and higher) and increases the amount of gas oil liquids, resid high in resins and asphaltenes require high pressures and large amounts of hydrogen and are thus not as attractive for hydroprocessing. Additionally heteroatoms, such as sulfur and metals that are prevalent in resins and asphaltenes, tend to poison hydroprocessing catalysts. On the other hand, thermal coking separates the polynuclear aromatic cores, which contain the majority of the heteroatoms, from their side chains. As the separated polynuclear aromatic cores convert to coke, the catalyst poisoning heteroatoms are concentrated in the coke, leaving the side chains as good material for further catalytic processing.

Heteroatom Compounds are compounds that are just not carbon or hydrogen, but include sulfur, oxygen, nitrogen, vanadium and nickel. Sulfur is found in small ring aromatics (SRA) with one or two rings as well as polynuclear aromatics that contain three or more rings. However, nitrogen, oxygen, vanadium and nickel are found chiefly in polynuclear aromatic (PNA) structures.

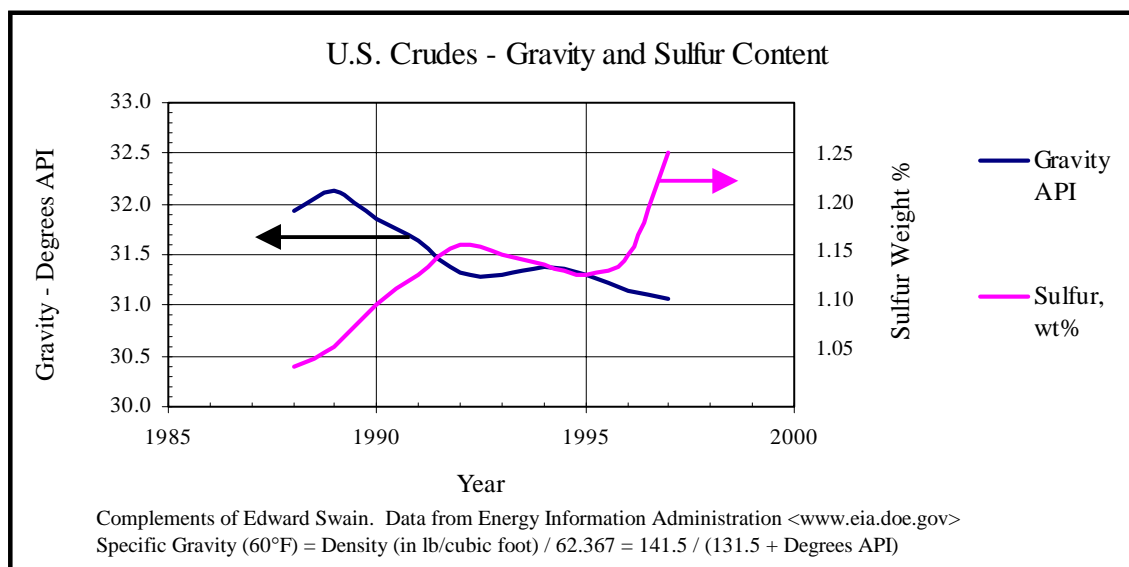
■ **Sulfur compounds** are one of the most important heteroatomic components and heavy crudes may contain up to 5% sulfur by weight. One investigation revealed almost 40 different sulfur compounds in one Texas crude. Sulfur is undesirable since it promotes corrosion, poisons refining catalysts, affects fuel odor and color stability,

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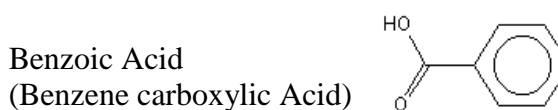
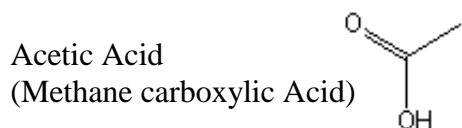
increases engine deposits, fouls engine catalytic converters and thus contributes to air pollution particularly carbon monoxide, hydrocarbons, and NOx. Two common sulfur compounds are ethyl mercaptan and thiophene.



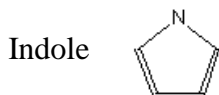
Since 1988, the apparent trend of sulfur (weight % sulfur) in crudes to U.S. refineries has been increasing concurrently with the increasing density of crudes to U.S. refineries. Although due to several reasons, these trends require refinery configurations suitable for processing heavier and higher sulfur crudes.



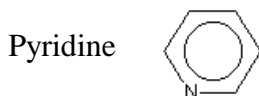
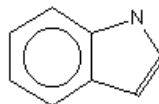
■ Oxygen compounds may occur in crudes up to approximately 2% by weight. The most investigated have been those with carboxylic groups. These may be alicyclic acids (naphthenic acids) or, less often, aliphatic acids. Alicyclic acids (naphthenic acids) tend to be found with hydrocarbons containing rings (example cycloparaffins or naphthenes) while aliphatic acids tend to be present with hydrocarbons without rings. This helps explain why oxygen compounds are found chiefly in polynuclear aromatic (PNA) structures. In virgin crudes, the existence of ketones, esters, ethers, alcohols, etc. is subject to some question. These may be due to long atmospheric exposure during production. Carboxylic acids are undesirable since they promote corrosion.



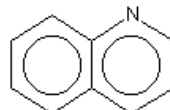
■ Nitrogen compounds may occur in crudes up to approximately 1% by weight. Nitrogen compounds are found chiefly in polynuclear aromatic (PNA) structures. Nitrogen is undesirable since it promotes corrosion, poisons refining catalysts, and contributes to gum formation in fuel. Typical examples of nitrogen compounds are illustrated.



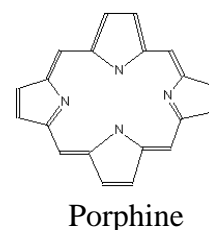
Pyrrole
(Benzopyrrole)



Quinoline
(Benzopyridine)



Another interesting groups of nitrogen compounds are porphyrins, the simplest of which is porphine. Porphyrins are important since they may be chelated with vanadium and nickel (the existence of iron chelates has not been definitely established) and are primarily contained in heavy crudes at concentrations of several thousand parts per million by weight. Vanadium porphyrins are more predominant in heavy sulfur crudes while nickel porphyrins are prevalent in low sulfur crudes.



■ Metals found in crude include vanadium, nickel, iron, copper, zinc, titanium and magnesium. Vanadium, nickel, iron and copper are present in the PPM (weight) level in polynuclear aromatic (PNA) structures of heavy crudes. Although it is known that vanadium and nickel exist as porphyrin complexes, some vanadium and nickel in crude exist as non-porphyrinic compounds. However there is disagreement about the relative percentage. Of the metals, vanadium and nickel are particularly undesirable since they poison refining catalysts and promote corrosion. Additionally the ash left after combustion in gas turbines and furnaces leaves deposits on gas turbine rotors and reacts with refractory linings of furnaces.

Very low concentrations of zinc, titanium and magnesium are found in metallic soap complexes at oil/water interfaces.

■ Crude oil also contains water-soluble inorganic sulfate and chloride salts, such as calcium, sodium, potassium, that are usually removed before atmospheric processing.