PETROLEUM

1. Origin

Petroleum is a naturally occurring complex mixture made up predominantly of carbon and hydrogen compounds, but also frequently containing significant amounts of nitrogen, sulfur, and oxygen together with smaller amounts of nickel, vanadium, and other elements. It may occur in solid, liquid, or gaseous form as asphalt (qv), crude oil, or natural gas (see GAS, NATURAL), respectively. The economic importance of crude oil and natural gas has stimulated considerable interest in their origin. Because of their fluid nature petroleum phases are mobile in the subsurface and may have accumulated far from the place where they formed. Herein, origin of petroleum means the combined processes that operate in nature and culminate in the petroleum that is present as commercial accumulations in permeable and porous reservoir rocks. The processes involved are petroleum generation, which occurs in the source rock; migration out of the source rock and to the reservoir; and maturation and alteration which operate to change the composition of the petroleum after it has accumulated in the reservoir.

A biogenic origin for the carbonaceous material in petroleum is widely but not universally accepted. An inorganic origin of petroleum has been proposed (1,2) and there is a dualist theory incorporating both biological and inorganic aspects (3). However, because inorganic processes generate racemic mixtures, the presence of optically active compounds in oils, especially the multiringed cycloalkanes (naphthenes), provides strong support for a biological hypothesis. Oils also contain the so-called chemical fossils or biomarkers, compounds having characteristic molecular structures that can be related to living systems. The compounds include isoprenoids, porphyrins, steranes, hopanes, and many others. The relative abundances of members of homologous series are often similar to those in living systems. The strong odd preference in the long-chain normal alkanes (C_4) is particularly well documented (4). In addition, the lack of thermodynamic equilibrium among compounds (5), and the close association of petroleum with sedimentary rocks formed in an aqueous environment, suggests a low temperature origin. In this context, low temperature means less than a few hundred degrees Celsius as opposed to temperatures in the 700–1200°C range that characterize igneous processes involving silicate melts. The elemental composition of petroleum (C,H,N,S,O), the isotopic composition of oils, and the presence of petroleum-like materials in more recent sediments are consistent with a low temperature origin. The evidence supporting a biological source for the material that generates petroleum is extensive (6–8).

Organisms produce a wide range of organic compounds including significant amounts of biopolymers like proteins (qv), carbohydrates (qv), and lignins (see LIGNIN), together with a wide variety of lower molecular weight lipids (6–8). After the death of the organism, all or part of this organic material may accumulate in aquatic environments where the various compounds have very different stabilities. Some are metabolized in the water column by other organisms (including bacteria) and only the biochemically resistant material is incorporated into sediments. Survival of organic material depends on many factors but particularly the oxidizing or reducing nature of the system. Preservation is strongly favored in anoxic sediments (9). However, the formation of a petroleum accumulation requires more than just a concentration of the relatively low molecular weight hydrocarbons that are present in more recent sediments. Although C_2–C_{10} hydrocarbons are present in extremely low (parts per billion (ppb) level) concentrations in organisms and sediments, these can account for up to 50% or more of the volume of some crude oils.

Compounds that are not synthesized by organisms are also reported in crude oils. Apparently these were formed from the available organic matter in what is thought to be the main process of petroleum generation. As the organic matter in sediments is buried in a reducing environment, and subjected to gradually increasing temperature and pressure, petroleum is generated as an intermediate in a transformation process that ultimately leads to methane and graphite. Oxygen is first lost from the organic matter as carbon dioxide and water. Continued low temperature ($<$°C) rearrangement takes place and the immature organic matter is converted to high molecular weight, insoluble material called kerogen. This becomes more aromatic and carbon-rich as it generates petroleum and evolves toward graphite. In contrast, the solvent-extractable lower molecular weight organic materials called bitumen or extractables increase in hydrogen content and progress through compositions typical of crude oils to those of gas (10).

The nature of organic material (kerogen) in source rocks controls whether oil or gas is generated, and also controls the composition of these products. In many cases, the type of organic matter can be recognized by microscopic examination after removing the mineral matrix with hydrofluoric and hydrochloric acids. Lignin-rich wood-derived materials appear to generate gas; surface coatings of plants that are rich in cutin and esters of long-chain acids and alcohols produce waxy oils that frequently have high pour points; organic matter derived from algae and other aquatic organisms seems to produce the normal range of crudes (6–8). Algal debris is frequently amorphous. The principal organic matter types can be identified because these produce distinct tracks across an atomic H/C versus atomic O/C diagram, the so-called van Krevelen diagram (11). With rising temperature, generally produced by increasing depth of burial, both the H/C and O/C atomic ratios decrease as the kerogen increases in carbon content. Much of the amorphous kerogen is hydrogen-rich and oxygen-poor, whereas the woody type is oxygen-rich and hydrogen-poor.

The relative amounts of the various types of organic matter is controlled by the environment where the sediments were deposited. For example, rivers transport lignin and surface coatings derived from land plants to the marine environment. As a consequence deltas are gas-prone environments (12) that frequently contain high pour-point crude oils rich in long-chain alkanes (13,14). Source rocks containing low percentages of organic matter generate insufficient oil to drive migration. The oil remains in the rock and is subsequently cracked to gas, so that poor source rocks only expel gas regardless of the organic matter type.

The ratio of bitumen to kerogen in sediments is initially low, but increases with depth of burial. It was shown in 1965 (15) that in the Los Angeles basin the increase becomes significant below about 3350 m, but in the adjacent Ventura basin the increase occurs deeper at about 4575 m. The geothermal gradients are different in these two basins, but the marked increase in bitumen:kerogen ratio occurs at the same temperature in both of them. Because the generation of bitumen from kerogen is the process of petroleum generation, this demonstrated clearly the important role of temperature. It also implied a minor (if any) role for pressure which differed by more than 50% between the two basins. Subsequent analyses of samples from many wells worldwide have shown similar trends. Wells have relatively low bitumen:kerogen ratios for the shallower section and rapidly increasing values deeper (7).

The petroleum generation process can be duplicated by laboratory pyrolysis. Higher temperatures are needed to produce these reactions in a few hours or days rather than the millions of years in nature (16,17). Both dry pyrolysis and hydrous pyrolysis have been used.

The generation of petroleum is nonbiological, induced by temperature, and influenced by available time. It follows essentially first-order kinetics (18) where an increase of 10°C roughly doubles the reaction rate at low temperatures. The low molecular weight compounds generated from the kerogen show none of the biological characteristics typical of compounds in more recent sediments. Therefore, at increasing depth, and hence increasing temperature, the bitumen fraction loses features such as odd–even predominance in long-chain normal alkanes, optical activity, and the predominance of four- and five-ringed cycloalkanes (11). These trends have been well-documented in many areas. The petroleum generation process can be treated quantitatively using models based on first-order kinetics (19). The Lopatin approximation (20) seems to give reasonable values for the onset of oil generation when properly calibrated (21), but more rigorous methods that treat generation as a series of parallel first-order reactions are more reliable (18,22–25).

An important exception to thermal generation is the bacterial formation of methane. The bacteria are anaerobic and effective in sulfate-free, anoxic conditions (26), and have long been recognized for their role in forming marsh gas. Bacterially produced methane is isotopically light, generally more negative than −55 parts per thousand (expressed as −55‰) for carbon, relative to the Pee Dee Belemnite (PDB) standard, and contains only trace amounts of ethane and higher hydrocarbons. This methane may, however, have higher amounts of inorganic gases. Many of the huge natural gas accumulations in Siberia, including the giant Urengoy field which has reserves of 5.9×10^{12} m^3 (210 Tcf), are thought to be bacterially generated. These accumulations are usually shallow, are isotopically lighter than −59‰ (27), and have only a percent or less of higher hydrocarbons. Examples are also known from other parts of the world (28–30).

Most petroleum is found in reservoir rocks that have high permeabilities and porosities, where these properties have been developed by natural processes of sorting and winnowing that remove fine-grained particles, including organic materials. Reservoir rocks generally have insufficient organic matter to generate commercially significant quantities of petroleum (see OIL SHALE). It is believed that petroleum generation occurs in organic-rich source rocks, and that part of the bitumen then migrates to accumulate in reservoir rocks (6,7). This is the source rock concept. Clearly, migration has a critical role in linking the organic-rich source rocks to the reservoir. Solubilities of hydrocarbons in subsurface waters are generally too low to be significant in the petroleum migration process (31,32), and most recent studies have stressed the expulsion of a separate crude oil phase out of source rocks (33,34). It appears that source rocks develop high internal petroleum saturation caused by petroleum generation and the displacement of water during compaction (35,36). Upon continuing compaction and kerogen conversion, oil droplets are forced out of source rocks into adjacent permeable carrier beds. High pressures approaching the rock load (lithostatic) can develop, and induce near-vertical fractures that are important in providing migration pathways out of the source rock. In this case the pressure gradient that develops can overcome buoyancy, and oil may be expelled downward and out the bottom of source rocks, as well as out of the top. The alkanes are less strongly absorbed in the source rock and so are preferentially expelled. In contrast, the nitrogen–sulfur–oxygen compounds (NSOs) are most strongly adsorbed and thus depleted in the expelled oil (37). Migration efficiency varies widely and appears to be dependent on the organic matter content of the rock. High efficiencies are associated with high organic contents. The controlling factor is hydrocarbon (bitumen) saturation, and rocks having less than about 1.0 wt % organic matter do not generate sufficient bitumen. As a consequence no oil migrates from these rocks and they are not effective source rocks (18,38).

Buoyancy is the main driving force through the carrier beds and oils continue to move upward (toward shallower areas) until stopped at a slope reversal in a structural trap, or where permeability decreases as in a stratigraphic trap (39,40). Migration distances can be in excess of 100 km (35,39). Oil may be remobilized after its initial accumulation in the reservoir. Although in the simplest case this may involve only a simple relocation, it can lead to significant compositional changes if both gas and oil are involved. When an anticlinal reservoir is full to the spill point and has a gas cap over oil, any spilling off the bottom is oil, and the next shallower trap thus accumulates oil with no gas cap. This process of differential entrapment (41) leads eventually to oil in the up dip (shallower) reservoirs and gas in the deeper ones. Geological examples are given (42,43).

The composition of petroleum changes and evolves in the reservoir in response to changing conditions. Thermal maturation of crude oil is brought about by the increasing temperature that accompanies increasing depth of burial (44,45). Some large molecules are broken down into smaller fragments and the trend is for an increasing percentage of the lighter fractions as the oil progresses to lower densities in the sequence from oil, to lighter oil, to wet gas, and finally dry gas (46). The increasing hydrogen content implied by this sequence is provided by parallel reactions involving cyclization and aromatization. These residual molecules get steadily more aromatic and larger, and as the solvent properties of the oil change, these molecules are precipitated in the reservoir in a process called natural deasphaltening (47). The solid precipitate also takes with it much of the NSOs, nickel, and vanadium, so that the producible oil is of better quality.

Large changes in petroleum composition can be produced by contact with flowing water (48,49). As the water moves past the oil in the reservoir, most water-soluble components are removed. These include the light ends, particularly the small aromatics, leaving a tar layer at the oil–water interface. If the water brings bacteria and oxygen into contact with the oils at temperatures below approximately 70°C, substantial changes in crude oil composition can result (49–51). The aerobic bacteria preferentially consume normal alkanes and may convert waxy crudes of high pour points to naphthenic crudes of low pour points. The removal of low density compounds leaves a heavier oil enriched in sulfur and nitrogen compounds because heavier fractions resist bacterial degration and so accumulate in the residue. Water washing always accompanies biodegradation.

Biomarkers form a small percentage of bitumen and crude oils, but relative distributions and complex structures are modified by the various processes involved during petroleum generation and accumulation. These biomarkers are widely used for correlation studies, and for recognition and documentation of the progress of generation and maturation (52,53).

The overall petroleum system (54) that leads to the accumulation of oil and gas in natural reservoirs can be summarized as follows: organic matter is incorporated into sediments as these are deposited; possible shallow generation of biogenic methane; organic matter is converted to petroleum-like materials by the influence of increasing temperature with lower temperatures partially offset by longer times; part of the lower molecular weight material that is generated subsequently migrates from the source rock through permeable carrier beds to the reservoir; after the oil reaches the reservoir significant compositional changes may be produced by increasing temperature, water washing, and bacterial degradation.

2. Composition

Petroleum, literally rock oil, describes a myriad of hydrocarbon-rich fluids present in source rocks and accumulated in subterranean reservoirs (see HYDROCARBONS C1–C6). Petroleum can include three phases: gaseous (natural gas), liquid (crude oil), and solid or semisolid (bitumens, asphalt (qv), tars, and pitches) (55) (see COAL; GAS, NATURAL; TAR AND PITCH). The molecular composition of the liquid portion of petroleum contributing to the crude oil properties and behavior is discussed in this section. Crude oils vary dramatically in color, odor, and flow properties. These properties often reflect the origin of the crude. Historically, physical properties such as boiling point, density (gravity), odor, and viscosity have been used to classify oils (2–4). Crude oils may be called light or heavy in reference to relative density (or specific gravity). Light crude oils are rich in low boiling and paraffinic hydrocarbons; heavy crude oils contain greater amounts of high boiling and asphalt-like molecules. The heavy oils tend to be more viscous, higher boiling, more aromatic, and contain larger amounts of heteroatoms. Likewise, odor is used to distinguish between sweet or low sulfur, and sour or high sulfur, crude oils.

The distribution of biomarker isomers, molecules that retain the basic carbon skeletons of biological compounds from living organisms, serves not only as a set of fingerprints for oil–oil and oil–source correlation (to relate the source and reservoir for exploration), but also to give geochemical information on organic source input (marine, lacustrine, or terrigenous source), age, maturity, depositional environment (clay or carbonate, oxygen levels, salinity, etc), and alteration (water washing, biodegradation, etc) (56,57).

Knowledge of the composition of petroleum allows the refiner to optimize conversion of raw petroleum into high value products (58). Originally, petroleum was distilled and sold as fractions, primarily for use in illumination and lubrication (see LUBRICATION AND LUBRICANTS). Crude oil is sold in the form of gasoline (see GASOLINE AND OTHER MOTOR FUELS), solvents (see SOLVENTS, INDUSTRIAL), diesel and jet fuel (see AVIATION AND OTHER GAS TURBINE FUELS), heating oil, lubricant oils, and asphalts, or it is converted to petrochemical feedstocks (see PETROCHEMICALS, FEEDSTOCKS) such as ethylene (qv), propylene (qv), the butenes, butadiene, and isoprene. Modern refining uses a sophisticated combination of heat, catalyst, and hydrogen (qv). Conversion processes include coking, hydrocracking, and catalytic cracking to break large molecules into smaller fractions; hydrotreating to reduce heteroatoms and aromatics, thereby creating environmentally acceptable products; and isomerization and reforming to rearrange molecules to those having high value, eg, gasolines of high octane number.

A knowledge of the molecular composition of a petroleum also allows environmentalists to consider the biological impact of environmental exposure. Increasingly, petroleum is being produced in and transported from remote areas of the world to refineries located closer to markets. Although only a minuscule fraction of that oil is released into the environment, the sheer volume involved has the potential for environmental damage. Molecular composition can not only identify the sources of contamination but also aids in understanding the fate and effects of the potentially hazardous components (59).

Crude oils contain an extremely wide range of organic functionality and molecular size. The variety is so great that a complete compound-by-compound description for even a single crude oil is not likely. The composite molecular composition of petroleum can, however, be described in terms of three classes of compounds: saturates, aromatics, and compounds bearing the heteroatoms sulfur, oxygen, or nitrogen. Within each of these classes there are several families of related compounds. Table 1 lists some of the compounds typically found in petroleum crude oils. Structures are shown in Figure 1. The saturates include normal alkanes, branched alkanes, and cycloalkanes called paraffins, isoparaffins, and naphthenes, respectively (see NOMENCLATURE IN THE PETROLEUM INDUSTRY). Alkenes (olefins) are rare to the extent of being considered an oddity. Aromatics range from benzene to multiple fused-ring analogues such as naphthalene, phenanthrene, etc. Sulfur is found in both polar (thiol) and nonpolar (thioether and thiophenic) forms (60). The nitrogen and oxygen compounds are more likely to be found in polar compounds such as pyridines, pyrroles, phenols, carboxylates, amides, etc, than in nonpolar ones such as ethers (61). The distribution and characteristics of these molecular species account for the rich variety of crude oils.

2.1. Elemental Composition. On an atomic basis, H/C ratios range from 1.5–2.0. The range of elemental composition of crude oil (16) may be given as follows:

Element	Composition range, wt %
carbon	84–87
hydrogen	11–14
sulfur	<0.1–8
oxygen	<0.1–1.8
nitrogen	<0.1–1.6

Nickel and vanadium are also generally present from a trace amount up to 1000 ppm. The value of using sulfur for petroleum classification can be clearly seen. Whereas the range of hydrogen and carbon are quite narrow, sulfur, the principal heteroatom in crude oil, varies significantly. The ranges for the other two heteroatoms (O and N) are also fairly wide, however in most crude oils these elements are nearly an order of magnitude lower than the sulfur level (Fig. 2). For example, the average level of nitrogen in >9000 crude oils is 0.094%, the average sulfur content is 0.65% (7). Although >90% of crude oils have nitrogen levels <0.2%, some crude oils have > 1.5% nitrogen. As noted in Figure 2**b**, the nitrogen concentrates into the highest boiling fractions. The trace metals Ni and V are generally orders of magnitude higher than other metals in petroleum, unless it is contaminated with coproduced brine salts (Na^+, Mg^{2+}, Ca^{2+}, Cl^-) or iron corrosion products gathered in transportation.

2.2. Molecular Classes. The molecules in crude oil include several basic structural types (Table 1, Fig. 1). Because they may contain from 1 to 100+ carbon atoms and may occur in combination, the statistical potential for isomeric structures is staggering. For example, whereas there are just 75 possible paraffinic structures for C_{10}, there are $>10^5$ isomers for C_{20}. A few structures tend to dominate the distributions of each isomer group, however.

The inclusion of naphthene and other aromatic rings introduces two additional dimensions, increasing the number of hydrocarbon isomers even further. A three-dimensional array in which the molecules could be described in terms of the number of aromatic rings, the number of naphthenic rings, and the number of carbons in alkyl side chains has been proposed (61). Conceptually, this amounts to describing a three-dimensional molecular mountain for hydrocarbons. There is also the potential of constructing similar mountains for heterocyclics. The two-dimensional image in the naphthenic and aromatic dimensions has been projected using sidebars to indicate the variation in alkyl substituents among crude oils (7).

Molecular characterization of a whole oil is beyond the capability of most analytical techniques. Distillation (qv), however, can separate petroleum into molecular weight fractions that simplify the task. Pioneering work with this approach, sponsored by the American Petroleum Institute (API) starting in 1925, has led to the identification of hundreds of individual compounds in distillation fractions of a single crude oil (62). Developments in chromatography (qv) allowed oils to be fractionated by polarity as a second dimension. Under API sponsorship, the U.S. Bureau of Mines extended separations and measurement techniques to heavier fractions (63). At the same time, individual compounds have been isolated and quantified from increasingly higher boiling fractions

(64–67). Techniques have been developed that use combinations of classical open-column adsorption chromatography, gel permeation chromatography, and ion-exchange (qv) separations to isolate fractions in which compounds could be identified by mass spectrometry (qv).

Whereas neither distillation nor chromatography achieves perfect separations among groups, the fractions generated are amenable to molecular characterization (66,67). An elegant argument has been made for the use of distillation for primary separation which is combined with a solubility step to achieve the atmospheric equivalent boiling point (AEBP) scale that covers room temperature to 1370°C (68). Because the distillations simplify analytical complexity, the bulk of available molecular compositional data on petroleum has been generated on sets of fractions defined by boiling points as gases (C_1–C_4), naphtha (initial bp −210°C), mid-distillate (210–345°C), vacuum gas oil (345–565°C), and vacuum residuum (>565°C). The initial boiling point (ibp) of the naphtha depends on the amount of C_1–C_5 hydrocarbons dissolved in the oil. For characterization purposes, naphtha is usually depentanized so that the ibp is about 32°C. The material that boils above 345°C is referred to as atmospheric resid and is further distilled under vacuum into vacuum gas oil (VGO) and vacuum resid. Whereas the AEBP of the vacuum resid is >565°C, the actual temperature of distillation does not exceed 345°C to avoid thermal decomposition.

Crude distillations yield different quantities in each fraction. About the same amounts are distilled into the middle distillate and vacuum gas oil from conventional crude oils. More naphtha is distilled from light crude oils and more vacuum residuum is obtained from heavy crude oils (Fig. 3). The typical distribution of classes of petroleum compounds shows a significant shift with boiling point (Fig. 4). Whereas the lower boiling fractions are dominated by nonpolar saturated hydrocarbons that exist in limited isomeric forms, the higher boiling fractions increasingly contain a larger variety of classes, that have, in turn, an increasing number of possible isomers. As the boiling point increases, aromatic ring structures build in, first as naked rings, then more and more as rings having attached side-chain and naphthene ring carbons. Polar compounds, typically those having O and N functionality, that appear as trace impurities in the lower boiling fractions gradually become significant components in the higher boiling fractions. This is confirmed by the distribution of S and N in petroleum against boiling point (Fig. 2). The S, not including H_2S and the light sulfur compounds such as mercaptans and sulfides, present in petroleum gases, is more widely distributed than the nitrogen that concentrates in the highest boiling fraction. Not shown is the subtle decrease that occurs in H/C ratio with increasing boiling point reflecting the increasing number of aromatic ring types at higher boiling point. The metals, nitrogen, and oxygen are predominantly found in the higher boiling fractions rich in polars.

Analytical Approaches Different analytical techniques have been applied to each fraction to determine its molecular composition. As the molecular weight increases, complexity increasingly shifts the level of analytical detail from quantification of most individual species in the naphtha to average molecular descriptions in the vacuum residuum. For the naphtha, classical techniques allow the isolation and identification of individual compounds by physical properties. Gas chromatographic (gc) resolution allows almost every compound having less than eight carbon atoms to be measured separately. The combination of gc with mass spectrometry (gc/ms) can be used for quantitation purposes when compounds are not well-resolved by gc.

For the mid-distillates and vacuum gas oils (VGOs), class isolation and measurement techniques allow speciation of many compounds. In particular, multidimensional instrumental techniques have been applied. Capillary gc quantifies even closely related isomers. Element-selective detectors for gc are used to identify N, S, and O heterocompounds; gc/ms techniques are used to identify and quantify individual compounds or families of compounds. Characterization of families of compounds having similar degrees of unsaturation, expressed by z-number as in $C_nH_{2n+z}X$, where X represents heteroatoms, can be done by ms quantification (69). The combination of high performance liquid chromatography (hplc) and high resolution/low voltage ms has also been used to resolve overlaps between aromatic hydrocarbons and sulfur analogues as well as among isomers of alkyl aromatics and naphthenoaromatics (69). For VGOs ms techniques give semiquantitative results owing to the lack of reference compounds for calibrating relative sensitivities. Alternative techniques such as ultraviolet detection may be needed to distinguish among structural isomers (70,71).

The combination of chromatographic isolation followed by ms measurements has been extended well above 565°C into fractions of the vacuum resid (72–74). For fractions not amenable to that approach, techniques that provide average functionality data have been applied to describe petroleum composition (72). Established techniques such as titration for acidic and basic functionalities and for sulfur types, ultraviolet (uv) spectroscopy for aromaticity, and infrared (ir) spectroscopy for dipolar functionality have been supplemented with alternative instrumental techniques to expand the average database. These include nuclear magnetic resonance (nmr) for aromaticity, x-ray photoelectron spectroscopy (xps) for chemical bonding, and extended x-ray absorption fine structure (exafs) for atomic coordination environment, as well as improved Fourier-transform ir and Raman techniques for functionality (see INFRARED SPECTROSCOPY AND RAMAN SPECTROSCOPY; MAGNETIC SPIN RESONANCE; SPECTROSCOPY, OPTICAL). The individual average techniques do not provide molecular composition (75). On the other hand, these techniques can provide an average composition when used in combination. For those portions of the vacuum residua that are both nonvolatile and insoluble and hence not accessible to molecular speciation techniques, the alternative techniques are helpful.

Petroleum Gases and Naphtha Methane is the main hydrocarbon component of petroleum gases. Lesser amounts of ethane, propane, butane, isobutane, and some C_4+ light hydrocarbons also exist. Other gases such as hydrogen, carbon dioxide, hydrogen sulfide, and carbonyl sulfide are also present.

The naphtha fraction is dominated by saturates having lesser amounts of mono- and diaromatics (Table 2, Fig. 4). Whereas naphtha (ibp to 210°C) covers the boiling range of gasoline, most raw petroleum naphtha molecules have a low octane number and most raw naphtha is processed further, to be combined with other process naphthas and additives to formulate commercial gasoline.

Within the saturates in petroleum gases and naphtha, except for a few highly branched components in the C_8–C_{10} range, every possible paraffin from methane to normal decane (n-C_{10}) is present. Depending on the source, one of the low boiling paraffins may be the most abundant compound in a crude oil, sometimes reaching a concentration of several percent. The isoparaffins begin at C_4. Isobutane is the only isomer of n-butane. The number of isomers grows rapidly with carbon number so that there are 74 isomers of C_{10}. Some of the individual 2-methyl isoparaffins may be present in concentrations $>1\%$. Using instrumental techniques every possible isoparaffin in petroleum up to C_8 has been identified. Although complete resolution of all isomers $>C_8$ is beyond analytical capabilities, many of these compounds have also been identified.

In addition to the aliphatic (chain) molecules, the saturates contain cycloalkanes, called naphthenes, having mainly five or six carbons in the ring (Fig. 5). Methyl derivatives of cyclopentane and cyclohexane are commonly found in greater quantity than the parent unsubstituted structures and can be present at levels above 2% (7). Fused-ring dicycloalkanes such as decahydronaphthalenes (decalins) and hexahydroindans are also common, but nonfused bicylic naphthenes, eg, cyclohexyl cyclohexane, are not.

The numerous aromatics in petroleum naphtha begin with benzene, but the C_1–C_3 alkylated derivatives of benzene generally are present in larger amounts. Toluene concentrations may reach nearly 2%; the combined xylene isomers exceed 1%; benzene, however, rarely exceeds 1% of a whole crude oil (7). Although present in lesser concentrations, each of the alkyl benzene homologues through the 20 isomeric C_4 alkyl benzenes have been isolated from Ponca City crude, as have several of the C_5-derivatives (76). Benzenes having fused cycloparaffin rings (naphthenoaromatics) such as indan and tetralin have been isolated along with a number of their methyl derivatives. Naphthalene is included in the naphtha, whereas the 1- and 2-methyl naphthalenes and higher homologues of fused two-ring aromatics appear in the mid-distillate fraction.

Sulfur is the only heteroatom to be found in naphtha, and only at trace levels (Fig. 2). A systematic study of organic sulfur compounds in Wasson Texas crude, and to a lesser extent three other crude oils, culminated in the identification of over 200 compounds, most of which were in the naphtha fraction (24). However, the total of these compounds accounted for less than 1% of the sulfur in the whole crude. In sour petroleum naphthas, 50–70% of the sulfur can be found in the form of mercaptans, ie, thiols. Over 40 individual thiols have been identified, including all the isomeric C_1 to C_6 compounds plus some C_7 and C_8 isomers and thiophenol (77). In sweet naphthas, the sulfur is distributed between sulfides, ie, thio-ethers, and thiophenes. In these cases the sulfides may constitute more than 50% of the sulfur compounds in the form of both linear (alkyl sulfides) and five- or six-ring cyclic (thiacyclane) structures. Sulfur structure distribution mimics the hydrocarbons; ie, naphthenic oils having high cycloalkanes have high thiacyclane content, etc. Typical alkyl thiophenes in naphtha have multiple short side chains or exist as naphthenothiophenes (77). Though rare, methyl and ethyl disulfides have been confirmed to be present in some crude oils (78).

Mid-Distillates As is indicated in Figure 4, saturates remain the primary component in the mid-distillate fraction of petroleum, but aromatics, which include simple compounds having up to three aromatic rings, and heterocyclics are present and represent a larger portion of the total. Some raw middle distillates are used directly as kerosenes, jet fuels, and diesel fuels; others are cracked and hydroprocessed before use. Some compounds found in middle distillates are listed in Table 3. Within the saturates, the concentration of n-paraffins generally decreases regularly from C_{11} to C_{20}. The 2-methyl analogues are sufficiently unique to be seen as distinct peaks in gc analyses of mid-distillates. Few additional isoparaffins have been identified. However, the two isoprenoids (**30**) and (**31**) (see Fig. 6) are generally present in crude oils in sufficient concentration to be seen as irregular peaks alongside the n-C_{17} and n-C_{18} peaks in a gas chromatogram. These isoprenoids, believed to arise primarily as fragments of ancient chlorophyll [1406-65-1] have relevance, as simple biomarkers, to the genesis of petroleum. The distribution of pristane and phytane relative to the neighboring n-C_{17} and n-C_{18} peaks has been used to aid in the identification of crude oils and to detect the onset of biodegradation (6). The ratio of pristane to phytane has also been used for the assessment of the stage of oxidation/reduction of the environment in which ancient organisms were converted into petroleum (56).

Mono- and di-cycloparaffins having five or six carbons per ring constitute the bulk of naphthenes in the middle-distillate boiling range, decreasing in concentration as the carbon number increases (7). The alkylated naphthenes appear to have a single long side chain as well as one or more methyl or ethyl groups (79). Similarly substituted three-ring naphthenes have been detected by gc/ms (80). Generally, fused rings share just a single face; however, the highly symmetric multifused molecule adamantane and its alkyl-substituted homologues have been found (6,81).

The most abundant aromatics in the mid-distillate are mono-, di-, and trimethyl naphthalenes. Other one- and two-ring aromatics are undoubtedly present in small quantities as either naphtheno or alkyl homologues in the C_{11}–C_{20} range. In addition to these homologues of alkylbenzenes, tetralins, and naphthalenes, the mid-distillate contains some fluorenes and phenanthrenes, with traces of biphenyls (82). The phenanthrene structure is favored over that of anthracene structure (7).

The S-heterocyclics in the mid-distillate range are primarily the thiacyclanes, benzothiophenes, and dibenzothiophenes. There are lesser amounts of dialkyl–, diaryl–, and aryl–alkyl sulfides (81). Alkylthiophenes are scarce or absent, but some evidence exists for benzthiacyclanes (Fig. 6). As for the naphtha fractions, these sulfur species account for a minimal fraction of the total sulfur in the crude. Although only ppm levels of nitrogen are found in the mid-distillates, both neutral and basic nitrogen compounds have been isolated and identified in fractions boiling below 345°C (64). Pyrroles and indoles account for about two-thirds of the nitrogen. The remaining nitrogen is found in the basic pyridine and quinoline compounds. Most of these compounds are alkylated.

2.3. Vacuum Gas Oils.

As is indicated in Figure 4, saturates contribute less to the vacuum gas oil (VGO) than the aromatics, but more than the polars present at percentage, rather than trace, levels. VGO itself is occasionally used as a heating oil but most commonly it is processed by catalytic cracking to produce naphtha or by extraction to yield lubricant oils.

Within the VGO saturates, distribution of paraffins, isoparaffins, and naphthenes is highly dependent on the petroleum source. The naphthenes account for roughly 60% of the saturates in a normal crude oil. However, samples can be found having paraffins from <20 to >80%. In most samples, the n-paraffins from C_{20}–C_{44} are still present in sufficient quantity to be detected as distinct peaks in gc analyses. Some crude oils show a nearly symmetric pattern of peaks such that each carbon number is present in regular progression up to a maximum around C_{27}. Other crude oils show a similar distribution, but have preference for odd-numbered alkanes. Both the distribution and the selectivity toward odd-numbered hydrocarbons are considered to reflect differences in petrogenesis of the crude oils. Although *n*-paraffins are distinct in the gc, these usually account for only a few percent of the saturates measured by gc.

The bulk of VGO saturates consists of isoparaffins and especially naphthenes (Fig. 3). A few isoprenoid compounds, such as squalane, C_{30}; lycopane, C_{40}; and carotanes, C_{40}; have been detected. Analyses of petroleum waxes isolated from the saturates show a parallel lower level of 2- and 3-methyl alkanes as the most identifiable isoparaffins. Mass spectrometry techniques show that the naphthenes contain from one to more than six fused rings. Having an average carbon number of C_{32}, even the six-ring naphthenes have some alkyl substitution. For mono- and diaromatics, the alkyl substitution typically involves one long side chain and several short methyl and ethyl substituents. Some specific tetracyclic naphthenes, including steranes, and pentacyclic naphthenes, including hopanes, have been used as biomarkers (Fig. 7). These hopanes and steranes have also been used as nondegradable conserved internal markers for estimating biodegradation of crude oils during bioremediation processes (83).

The aromatics in VGO may contain one to six fused aromatic rings that may bear additional naphtheno rings and alkyl substituents in keeping with their boiling range. Mono- and diaromatics account for about 50% of the aromatics in petroleum VGO samples. Studies by nmr indicate an average of 3.5 substituents per monoaromatic, whereas ms techniques show the presence of up to four fused naphthenic rings on some aromatic compounds (71). This is consistent with the suggestion that these species originate from the aromatization of biogenic steroids (7,84). Although they are present at lower concentration, alkyl benzenes and naphthalenes commonly show one long side chain and multiple short side chains.

The fused 3+ ring aromatics in petroleum include both *cata*- and *peri*-condensed structures (see Table 4, Fig. 8). The *cata*-condensed species are those structures where only one face is shared between rings, the *peri*-condensed molecules are those that share more than one face. The fused ring aromatics form the class of compounds known as polynuclear aromatic hydrocarbons (PAH) which includes a number of recognized carcinogens in the 4+ ring family (85). Because of the potential health and environmental impact of PAH, these compounds have been studied extensively in petroleum.

The total levels of three–six ring PAH in a petroleum VGO fraction range from 2 to 25%. However, the concentrations of individual isomers that have been quantified are generally expressed in parts per million (ppm). Although the most abundant reported individual phenanthrene compounds appear to be the C_1–C_3 derivatives, the average carbon number for the phenanthrenes in a VGO is C_{32}, indicating that the average side chain actually has 18 carbon atoms. The analytical techniques that have been used to isolate individual compounds are biased toward the least substituted aromatic structures, ie, the techniques that facilitate identification of a few target compounds eliminate the majority of multiring aromatic compounds.

Within petroleum certain aromatic structures appear to be favored. For example, alkyl phenanthrenes outnumber alkyl anthracenes by as much as 100:1. In addition, despite the bias in separation methods, alkyl derivatives appear to be more abundant than the parent ring compounds. For larger ring PAH, patterns exist, but are more difficult to detect owing to analytical resolution limits for the increasing number of isomers. A survey of crude oils by ms suggests that chrysenes are favored over pyrenes. Even for larger ring systems, the carbon numbers show that the parent compounds are missing or present in trace quantities. The C_3 derivatives are most prevalent.

The heterocyclics are significant contributors to the VGO fraction. Assuming an average molecular weight of 320 for the VGO, sulfur levels of from 0.5 to $>2.5\%$ would indicate that from 5 to $>25\%$ of the molecules contain a sulfur atom (78). Results of API-60 show that 60% of the sulfur compounds are thiophenic and the remainder sulfidic. Although there is some contribution from alkylaromatic and diaryl sulfides, no dialkyl sulfides were detected. In contrast, from 20 to 36% of the sulfur compounds existed in thiacyclane structures of one to eight saturated rings. Gel permeation chromatography of the aromatic fractions coupled with ms led to identification of >30 homologous thiophenic series including 18 having more than a single sulfur atom. Although the distribution into these groups varied widely among crude oils, benzothiophenes, and dibenzothiophenes, having from zero to six naphtheno rings, were the prevalent thiophenic forms of sulfur, accounting for 30–40% of the total. Many of the homologous series appear to be *S*-analogues of the hydrocarbon PAH, ie, benzologues of dibenzothiophene, but no specific compounds have been isolated and identified unambiguously.

The nitrogen levels in crude oils are generally an order of magnitude lower than those of sulfur. In the VGO range, the nitrogen-containing compounds include higher molecular weight pyridines, quinolines, benzoquinolines, amides, indoles, and carbazoles; and molecules having two nitrogens, ie, diaza compounds, and three or four aromatic rings are especially prevalent (72). Typically, about one-third of the compounds are basic, ie, pyridine and its benzologues, whereas the remainder are present as neutral species such as amides and carbazoles. Although benzo- and dibenzoquinolines found in petroleum are rich in sterically hindered structures, hindered and unhindered structures have been found to be present at equivalent concentrations in source rocks. This has been rationalized as geo-chromatography in which the less polar (hindered) structures moved more readily to the reservoir (56).

Oxygen levels in the VGO parallel the nitrogen content. Thus, the most identified oxygen compounds are phenols and carboxylic acids, frequently called naphthenic acids. These may account for from ppm to nearly 3% of a VGO. The presence of numerous complex naphthenic and naphthenoaromatic acid structures in crude oils, especially immature forms, has been shown (86). Among the different structures a number of specific steroid carboxylic acids have been identified.

2.4. Vacuum Residua. The vacuum residua or vacuum bottoms is the most complex fraction. Vacuum residua are used as asphalt and coker feed. In the bottoms, few molecules are free of heteroatoms; molecular weights range from 400 to >2000, so high that characterization of individual species is virtually impossible. Separations by group type become blurred by the sheer mass of substitution around a core structure and by the presence of multiple functionalities in a single molecules. Simultaneously, the traditional gc and ms techniques require the very volatility that this fraction lacks.

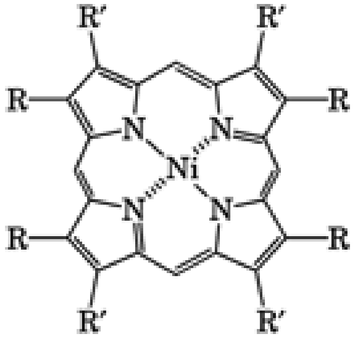
Classically, pentane or heptane precipitation is used as the initial step for the characterization of vacuum resid. The asphaltenes, the material that precipitates from the sample, range from 1 to 25% of vacuum resids. The soluble portion (maltenes) are then fractionated chromatographically into several poorly resolved classes for characterization. Asphaltene separations provide a simple way to remove some of the largest and most polar components; however, the fractions generated are still so complex that techniques such as nmr, titration, xps, or ir are mainly used to provide some average compositional detail. Asphaltenes are thought to be aggregates of complex molecular structures of MW <2000. The aggregation mechanism is not well understood. Evidence exists for both charge-transfer, among the numerous heteroatom functionalities, and φ–φ stacking of aromatics within the asphaltenes. The pitfalls of using average techniques for these complex systems have been discussed (73).

Additional general compositional information has been derived for the vacuum resid, using more sophisticated techniques that differ in approach toward isolating fraction. One approach uses functional group separations. Ion exchange (qv) has been used as the primary fractionation of vacuum resid into acids, bases, and neutrals (72,84). A second approach uses distillation into carefully defined atmospheric equivalent boiling points (AEBP) for the initial separation (73). Fractions generated by these separations have been subjected to a battery of techniques including liquid chromatography, field ionization mass spectrometry (fims), nmr, and elemental analyses.

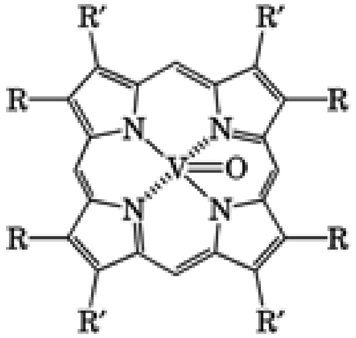
In fractions distilled above 565°C, the paraffins contribute only $<2\%$ of the 10–20% saturates. The one- to six-ring naphthenes contribute the rest, having average carbon numbers of 48–63. In the same study, aromatics shift progressively from an even distribution of mono- to tetraaromatics toward one dominated by five-ring types. As evidenced by the z-series data, many aromatics bear one or more naphtheno rings plus sufficient side-chain carbon atoms to bring the mean mol wt to nearly 800, ie, approximately 40 side-chain carbon atoms for a five-ring aromatic core of mol wt about 300. However, the elemental data show that 80% of the molecules could contain sulfur. Whereas most of the sulfur is thought to be thiophenic, studies by x-ray absorption spectroscopy have shown that in some vacuum resids it can exist in approximately equal amounts as sulfidic and thiophenic forms (87).

For the 565°+ fraction the levels of nitrogen and oxygen may begin to approach the concentration of sulfur. These elements consistently concentrate in the most polar fractions to the extent that every molecule contains >2 heteroatoms. At this point, structural identification is not attempted. Rather, average characterization techniques are used to confirm the presence of functionalities such as acids, phenols, carbazole, and benzoquinoline, found in lower boiling fractions. Several models have been proposed based on the observed functionalities, apparent molecular weight, and elemental analysis of the fraction. These models suggest that molecules having boiling points greater than 565°C consist of multiple units similar to lower boiling components linked together with carbon and sulfur bridges rather than ever-increasing fused-ring structures (88).

The Ni and V concentrated into the vacuum resid appear to occur in two forms. From 10 to 14% of each of these two metals can be distilled in the 565–705°C boiling range, where they exhibit the strong visible Soret bands associated with the porphyrin structure. This tetrapyrrole structure (**48,49**), possibly derived from ancient chlorophyll, has been confirmed by a variety of analytical techniques.



(48)



(49)

Because the metalloporphyrins can provide insights into petroleum maturation processes, they have been studied extensively, and several families of related structures have been identified. On the other hand, the bulk of the metals are found in the heaviest fraction. Because those highly polar fractions do not exhibit a Soret band, they are designated nonporphyrin metals. However, a number of techniques suggest that the metals in these Soret-inactive compounds still exist in molecules containing tetrapyrrole structures. Whereas other structures have been proposed (89), none has been demonstrated conclusively (90).

3. Nomenclature

Crude oils, complex mixtures of naturally occurring organic liquids, are difficult to characterize in detail. Thus, many of the definitions used by the exploration, production, and refining sectors of the petroleum industry to describe petroleum and its products often lack precision. Even the term petroleum is poorly defined. Although often used synonymously with crude oil, petroleum is also frequently used to include natural gas (see GAS, NATURAL) and even solid hydrocarbons. Definitions of materials are commonly given in terms of the processes used to obtain them. Gasoline, for example, is the fraction of crude oil that distills between 15 and 200°C (60 and 392°F) (see GASOLINE AND OTHER MOTOR FUELS). Further complications arise because different parts of the petroleum industry use terms in differing ways. For example, wax may refer to material made up predominantly of long-chain alkanes, or it may refer to esters of long-chain alcohols and acids (see WAXES). Even the term hydrocarbons (qv) is used loosely indicating all the compounds in crude oils, whether or not these include compounds of nitrogen, sulfur, and oxygen.

In nature petroleum occurs in subsurface accumulations, or reservoirs, called fields that may be made up of one or more pools. Petroleum compositions vary widely and range from hydrocarbon-rich gases called natural gas, through crude oil liquids, to high molecular weight solids known as reservoir bitumen, residual oil, or tar. Petroleum is generated from kerogen, the high molecular weight, insoluble organic material in source rocks. High subsurface temperatures convert the kerogen to a petroleum-like range of compounds called bitumen. Part of this bitumen moves out of the source rock, in the process of expulsion or primary migration, and moves through permeable rocks to accumulate in a reservoir (secondary migration). The petroleum engineering procedures for bringing this petroleum to the surface are called production.

Traditionally the unit of crude oil production has been the barrel (bbl), equal to 42 U.S. gallons, 5.61 ft^3, 158.8 L, or 0.159 m^3. Increasingly petroleum reserves are given in metric tons, but because one unit is a volume and the other a weight, there can be no unique conversion factor for a material having a range of densities. Fields of $>500 \times 10^6$ bbl (79.5×10^6 m^3) of recoverable oil ($>100 \times 10^6$ bbl (15.9×10^6 m^3) in the U.S.) are called giants. Oil density may be reported in any appropriate units, and although metric units are used it is more common to report densities as degrees API (°API) or API gravity, where API stands for American Petroleum Institute. The relationship between density and API gravity is an inverse one defined by the following relationship:

$$^{\circ}\text{API} = [141.5/\text{specific gravity at } 60^{\circ}\text{F}] - 131.5$$

Water corresponds to an API gravity of 10; crude oils fall between 10 and 60°API. The most common crude oil values are in the 35–40° range.

Other terms relating to physical properties include viscosity; refractive index; pour point, ie, the lowest temperature at which the oil flows; flash point, ie, the temperature at which the oil ignites; and aniline point, ie, the minimum temperature at which equal volumes of oil and aniline are completely miscible. These are determined under defined conditions established by ASTM.

Natural gas production is generally given in cubic feet or cubic meters (1000 $ft^3 = 1$ Mcf $= 28.3$ m^3). Reserves of a trillion cubic feet (Tcf) (28.3×10^{12} m^3) or more form a giant gas field. Natural gas is called dry when methane is the dominant hydrocarbon, and wet if it contains more than 4 L/100 m^3 of natural gas liquids (>0.3 gal/1000 ft^3). When gas (or oil) has a bad odor owing to high concentrations of hydrogen sulfide and volatile sulfur compounds it is called sour. Sweet gas has no noticeable odor. For statistical purposes gas is commonly reported as an equivalent amount of oil based on an equivalent heating capacity. The conversion is normally made using 170 m^3 (6000$ft^3 = 1$ bbl) and leads to a barrel of oil equivalent (boe).

Crude oils contain a wide range of hydrocarbons including straight and branched chains, ring compounds, and aromatics, as well as more complex compounds that incorporate nitrogen, sulfur, and oxygen (often called the NSOs), and some nickel and vanadium. The straight-chain, normal alkanes, range from 1 to >100 carbon atoms. These are often called paraffins in the petroleum industry because of the useful adjective paraffinic. Branched hydrocarbon chains that are nominally built up from repeated isoprene units (2-methyl butane structure) are called isoprenoids or terpenoids, and the 19- and 20-carbon compounds, named pristane and phytane, respectively, are frequently present in high concentrations. Isoprenoids also lead formally to saturated multiring structures. Petroleum chemists use the obsolete word naphthenes for the compounds that organic chemists call alicyclics. A better term, cycloparaffin, is used herein, leading to the adjective cycloparaffinic rather than naphthenic. Some of the characteristic structures in this group can be directly related to molecules synthesized by organisms. Whereas these have been called chemical fossils, it is more usual to call them biological markers or biomarkers. Common examples include the steranes and hopanes.

Aromatic hydrocarbons form a minor but important group of compounds in crude oils and range from single-ring to multiring compounds. The latter are called polycyclic aromatics (PAHs). Small aromatic molecules are environmentally significant and BTEX is commonly used as an abbreviation for benzene–toluene–ethyl benzene–xylenes. Multiringed compounds containing both aromatic and saturated rings may be referred to in the older literature as naphtheno-aromatics. The highest molecular weight fraction of crude oils commonly contains ashphaltenes that are dark in color, NSO-rich, and very aromatic.

Most crude oil is refined to provide useful products and the dominant process is distillation (qv) (Table 5). Petroleum products produced by simple distillation without the use of pressure, cracking, or catalysts are called straight run. Residual material that has too high a molecular weight to distill forms a residuum, often called by such names as asphalt (qv). Naphtha (unrelated to naphthenes) is a distillate of petroleum having a boiling range lower than about 200 or 260°C (even occasionally up to 350°C). As a process intermediate, naphtha includes the components used to formulate gasoline and the lighter grades of fuel oils such as kerosene and diesel fuel oil. As a finished product, naphtha usually denotes a more specific type of narrow boiling range material. The terms naphtha and solvent may be used interchangeably. For example, Varnish Makers' & Painters' (VM&P) naphtha has a range of 95–150°C. The majority of streams within a refinery designated as naphthas are straight-run materials, however the term can also be used for some cracked distillates.

A number of other words that have traditionally been used in the petroleum industry are difficult to define precisely. These refer partly to specific boiling ranges, but also to certain intended uses. Thus, gasoline boils lower than naphtha, and kerosenes generally higher, but these terms are applied to products that are intended as fuels, rather than as solvents.

Gas oil is a product boiling slightly higher (235–425°C, or sometimes wider) than kerosene. The main feedstock to the catalytic cracking units (see FEEDSTOCKS, COAL, CHEMICALS), it received its name from use as an enriching agent in the production of city or manufactured gas. It is often used as diesel fuel.

Cylinder oil is a viscous oil used for lubricating the cylinders and valves of steam engines (see LUBRICATION AND LUBRICANTS). It is prepared from cylinder stock. The product from cylinder stock, when filtered and processed, is bright stock.

Cycle stock (recycle stock) denotes any product that is recycled, that is, taken back to an earlier stage in the process. The term cycle stock is also used for the gas oil-like product of catalytic cracking.

The word distillate is occasionally used by petroleum chemists with a specialized meaning. Although anything that has been distilled is, of course, a distillate, the term distillate is sometimes used to denote distillate fuel oil as opposed to residual fuel oil.

In the petroleum industry the International Union of Pure and Applied Chemistry (IUPAC) system is in widespread use for naming organic compounds. Two points, however, regarding group names and the prefix, iso, call for comment.

3.1. Group Names. Although the IUPAC system is effective in denoting any hydrocarbon, no matter how complicated, the system does not always result in convenient terms for groups of compounds. Because hydrocarbons having the same number of carbon atoms are apt to have boiling points within a small range, it would be convenient to have words that would refer to C_4, C_5, C_6, ... saturates, and C_4, C_5, C_6, ... monounsaturates, etc. The IUPAC system, however, goes by the number of carbon atoms in the longest straight chain. Thus, for example, the hydrocarbon referred to by the older systematic name of isobutane, when named in the IUPAC system is 2-methylpropane. However, for saturated aliphatic hydrocarbons, names such as butanes, pentanes, hexanes, etc, are taken as names in the older system, and therefore used as group names.

The situation is different when naming the ethylenic hydrocarbons, because the IUPAC has provided names such as propene, butene, and pentene, which are different from the former names ending in -ylene. However, butenes/butylenes, pentenes/pentylenes, etc, are not truly synonymous pairs, because the IUPAC name goes by the longest-chain rule. Isobutylene, named 2-methylpropene in the IUPAC system, would be included under substituted propenes, but not under butenes. Similarly the three pentylenes derived from isopentane are methylbutenes and not pentenes. For example, if it is necessary to denote the group of five isomeric monounsaturated hydrocarbons C_5H_{10}, the term pentylenes denotes this group, whereas pentenes denotes a narrower group having only two members, the two straight-chain pentylenes.

3.2. The Prefix Iso. In names such as isobutane, isopentane, isobutyl alcohol, and isoamyl alcohol, the prefix iso has a precise meaning, ie, one methyl group attached to the next-to-terminal carbon atom and no other branch. This notation is also frequently used by petroleum chemists to have a much wider meaning, denoting nothing more than branched-chain. If both meanings persist, any individual use of the prefix becomes ambiguous. Herein, an effort is being made to use branched-chain or just branched consistently for the looser meaning of iso, so that this prefix can be kept for denoting concisely what otherwise would require some circumlocution. An exception is made for the well-established name isooctane, which is 2,2,4-trimethylpentane [540-84-1].

4. Petroleum Resources

Petroleum resources are distributed widely in the earth's crust as gases, liquids, and solids. The products derived from these naturally occurring resources are used principally as energy sources, although substantial volumes serve as feedstocks in the chemical, plastics, and other industries (see FEED STOCKS, COAL, CHEMICALS). Petroleum resources are found as natural gas, as a variety of liquids that are usually classified as normal or heavy crude oils, and as semisolid and solid substances such as asphalt (qv), tar, pitch, gilsonite, and many others. The petroleum resources considered here are those liquid crude oils that can be produced through a conventional wellbore by current primary, secondary, or tertiary (enhanced recovery) production techniques and those unconventional crude oils that may be captured and converted into conventional sources of crude petroleum by advancing production technologies.

No method has been devised to estimate with complete accuracy the amount of crude petroleum that ultimately will be produced from the world's conventional oil and gas fields. Degrees of uncertainty, therefore, should be attached to all such estimates. These uncertainties can be expressed in several ways, the most important of which is achieved by dividing a resource into various categories. Several petroleum resources classifications have been proposed, and a comprehensive discussion of them (91), as well as the definition used in the assessment of the undiscovered resources of the United States (92), have been provided. Seven commonly used categories of resources are given here.

Resources represent the total amount (including reserves) of petroleum that exists in a form and amount such that economic extraction is currently or potentially feasible.

Reserves constitute the petroleum that has been discovered and can be produced at the prices and with the technology that exist when the estimate is made.

Proved reserves are estimates of petroleum reserves contained primarily in the drilled portion of fields.

Indicated reserves constitute known petroleum that is currently producible but cannot be estimated accurately enough to qualify as proved.

Inferred reserves are producible, but the assumption of their presence is based on limited physical evidence and considerable geologic extrapolation. This places them on the borderline of being considered undiscovered, and the accuracy of the estimate is very poor.

Subeconomic resources constitute the petroleum in the ground that cannot be produced at present prices and technology but may become producible at some future date at higher prices or by improved technology.

Undiscovered resources are estimated totally by geological reasoning; no evidence through drilling is available.

To various degrees, the conventional petroleum resources in many parts of the world have been classified according to such a system. In certain regions, only estimates of proved reserves are made routinely, whereas in the United States, Canada, and certain other regions, estimates are made of volumes of petroleum in each of these categories. In the United States and Canada, estimates for several of these categories (in particular, proved reserves) are made each year by governmental agencies. For other categories, eg, undiscovered U.S. resources, many estimates have been prepared by various agencies, committees, panels, and companies. In a similar manner, estimates for several resource categories have been made for most other countries and for the world as a whole.

4.1. World Reserves.

Most of the large volume of crude petroleum consumed in the world is extracted from only a small fraction of the total number of oil fields discovered. The concentration of crude petroleum in a few large fields is a consequence of the interaction of the geologic processes that create and trap petroleum. Even though commercial quantities of petroleum have been discovered in many localities around the world, there are enormous volume differences in fields present in a single region and in the total volume of petroleum present in different regions.

By far the largest known concentrations of conventional petroleum reserves are in the Middle East, particularly in Saudi Arabia, the United Arab Emirates, and Kuwait. The largest concentration of reserves is in the Burgan field (10.2×10^9 m^3 (64.2×10^9 bbl)) in Kuwait (10), which contains about 68% of that country's reserves. The second largest concentration of reserves is in the Ghawar field (7.4×10^9 m^3 (46.5×10^9 bbl)) in Saudi Arabia (93), which is about 18% of that country's reserves. In some regions, a large portion of the reserves may not be contained in the largest field. However, the largest field usually contains more than 10% of the total reserves of a region. More than 20,000 petroleum fields have been discovered worldwide, and more than half of the world's proved reserves of ca 160.1×10^9 m^3 (1006.8×10^9 bbl) of petroleum are contained in only the 51 largest fields (93).

The Energy Information Administration estimates U. S. oil and gas reserves, but does not systematically estimate worldwide reserves. They have published a listing of international reserves as presented in two widely circulated trade publications (Table 6). The world's oil reserves are estimated to be 1.16 trillion barrels. The United States ranks 11th in the world for proved reserves of crude oil. World reserves increased about 4% in 2003 owing to the addition of former Soviet Union states.

Other large reserves other than Saudi Arabia's are located in Iraq, whose reserves are almost five times larger than that of the United States, Venezuela and Canada have triple the amount.

4.2. United States' Reserves.

The United States had the following proved reserves as of December 31, 2003: crude oil, $21{,}891 \times 10^6$ barrels; dry natural gas, $189{,}0444 \times 10^9$ ft^3; and natural gas liquids, $7{,}459 \times 10^6$ barrels (94). Table 7 listed the estimated annual oil reserve balances since 1993.

Crude oil proved reserves, reserve changes and production for individual states for 2003 are listed in Table 8.

Proved reserves of crude oil decreased by 786×10^6 barrels in 2003. Total discoveries are those reserves attributable to field extensions, new field discoveries, and new reservoir discoveries in old fields.

The majority of crude oil total discoveries were in new field discoveries in the Gulf of Mexico Federal Offshore. New field discoveries accounted for 705×10^6 barrels of crude oil additions, 702×10^6 were in the Gulf of Mexico. Operators discovered 426×10^6 barrels in extensions in 2003. This total was

13% less than the previous year. New reservoir discoveries in old fields were 101×10^6 barrels, 34% less than the previous year.

Reserve additions are the sum of total discoveries, revisions, and adjustments, and sales and acquisitions. In 2003 there were $1{,}091 \times 10^6$ barrels of reserves additions, 48% less than the previous year.

The smaller than average volume of net revisions and adjustments and negative net of sales acquisitions of crude oil proved reserves significantly reduced reserves additions in 2003. Crude oil net revisions and adjustments were 257×10^6 barrels, 77% less than 2002.

Production was estimated at $1{,}877 \times 10^6$ barrels in 2003.

4.3. World Petroleum Supply and Consumption. Historically, the world's petroleum production pattern can be related to geologic, economic, and political factors. In the past, many countries have had large excesses in production capacity, whereas since the 1990s, only countries in the Middle East, such as Saudi Arabia, Kuwait, Iraq, and the United Arab Emirates, have, in the short run, enough excess capacity to expand production of conventional crude petroleum in any significant manner. In the Middle East, production of petroleum is over five times the region's consumption. On a much smaller scale, Africa produces far more petroleum than it consumes. See Table 9 for world supply and consumption projected out of 2025.

4.4. Outlook. Petroleum displaced coal (qv) as the principal source of energy in the United States by 1948 and in the world by 1965 (99). The spectacular growth in consumption of crude petroleum in the world during the middle and late twentieth century is directly attributable to the ease with which petroleum can be discovered, produced, transported, processed, and utilized (see ENHANCED OIL RECOVERY). This growth has been so rapid that as much crude petroleum (55.5×10^9 m^3 (349.4×10^9 bbl)) was taken from the ground between 1976 and 1992 as was produced during the entire previous 119-yr period (1857–1975). This rapid rate of expansion in production and consumption, coupled with the finiteness of the conventional petroleum resource base, has from time to time led some analysts to conclude that world petroleum production will peak in the near future (100,101). Other analysts who examine such data forecast impending global crisis as crude petroleum consumption declines and coal reclaims its former position as the principal source of fossil energy (102).

The key factor influencing the varying interpretations is that although there is an enormous volume of petroleum resources in the ground throughout the world, it is found in deposits that differ in quality and quantity from country to country. Only a small fraction of these resources are conventional petroleum resources (160.1×10^9 m^3 (1006.8×10^9 bbl)) and are in the category of proved reserves. An additional 93×10^9 m^3 (585×10^9 bbl) of conventional petroleum is estimated to be undiscovered in the world. This estimate is of undiscovered petroleum resources that are economic to produce by means of normal production technology.

Although the world is not running out of petroleum, it is difficult to sum up how much is available in the short run, as well as in the longer run, in light of various possible future political and economic developments. The effect of a variety of sociopolitical forces now at work will be to reduce the world's consumption of energy, in particular of petroleum; such forces include clean-air regulations in the United States and the ever-increasing rate of taxation of petroleum use in many countries in order to raise general revenues. Countervailing forces, such as the advancement of exploration and production technology, can be counted on to expand the discovery and development of additional conventional petroleum resources in deep-water offshore regions and in hostile arctic climates. Also, advancements in technology, eg, in three-dimensional seismic surveys and horizontal drilling, will increase the inventory of proved reserves through the process of field extensions. Over the next several decades, many billions of cubic meters of conventional petroleum will be credited to the reserves inventory through this field-growth process. Table 10 gives an estimate of world oil resources for the years 1995–2025 (98).

Perhaps the biggest contribution that technological advancement in petroleum production will make is bringing large volumes of unconventional petroleum resources, eg, heavy oil and tar sands, into a viable economic realm by lowering the unit cost of production. Compared to the inventory of conventional petroleum reserves and undiscovered resources, the physical inventories of such unconventional petroleum resources are extremely large; for example, the Athabasca tar sands in Alberta, Canada, are estimated to contain 360×10^9 m^3 (2250×10^9 bbl) of in-place petroleum (103). This volume is equivalent to the total inventory, ie, the combined cumulative production, reserves, and undiscovered resources, of world conventional crude petroleum. In 1992, however, only about 10% of total in-place petroleum resources was technically recoverable (104).

Large unconventional resources of petroleum also occur as extra heavy crude oils in the Orinoco belt, Venezuela, and in oil shale in the western United States. Petroleum resources in the unconventional category, such as tar sands, heavy crude oils, and oil shales, are located mostly in the Western Hemisphere, as opposed to the conventional resources, which are located mostly in the Middle East. Also, the in-place resources of these unconventional resources are about twice as large as the in-place resources of conventional crude petroleum. Although the recovery rates from these resources are low, improving technology may capture increasing volumes of these unconventional petroleum resources, thereby converting them into conventional petroleum resources.

The irony underlying the current perceptions of the world's petroleum resource situation is that the world is not running out of combined petroleum resources. However, the bulk of the world's conventional petroleum resources that are inexpensive to produce are concentrated in the Middle East, whereas the much larger volume of higher cost unconventional petroleum resources, such as tar sands and heavy oils, are located in Venezuela, western Canada, and the western United States. The uneven distribution of the conventional resources thus causes concern that in the short run political unrest in the Middle East could cause a catastrophic interruption of supply.

The world will never "run out" of petroleum, simply because there is so much of it in the ground in so many different forms. However, the resources of conventional crude petroleum are finite. These are the petroleum resources that are very inexpensive to produce because they flow to the wellbore either directly or by pumping after the application of standard well completion methods. There is a more or less general agreement among analysts that the size of the inventory of these resources is about 350×10^9 m^3 (2200×10^9 bbl); the world is consuming these resources at about 1%/yr. The primary question that faces the world is, "Has the pattern of exponential growth in consumption of petroleum that took place between the end of World War II and 1973 become a relic of the past, or could growth resume as world population continues to expand?" Analysis of the pattern of world energy consumption shows that the world consumption of crude petroleum may gradually increase even with increased efficiency in the use of energy, simply as a result of population growth. However, these developments could be dramatically altered by an increase in the price of energy (105,106).

Another consideration of petroleum assessment analysts is whether, and to what degree, the vast resources of unconventional petroleum in the world can be captured by advances in petroleum production technologies, thereby converting them into conventional sources of petroleum. It is a simple fact that the in-place resources of petroleum in tar sands, heavy oils, and oil shale can guarantee the future supply of petroleum for hundreds of years at the current rate of consumption, provided they can be produced at competitive costs.

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Table 1. **Compounds Found in Petroleum Crude Oils**[a]

Compound	CAS Registry Number	Molecular formula	Structure number
Saturates			
n-octane	[111-65-9]	C_8H_{18}	(1)
2-methyloctane	[3221-61-2]	C_9H_{20}	(2)
propylcyclohexane	[1678-92-8]	C_9H_{18}	(3)
Aromatics			
n-butylbenzene	[104-51-8]	$C_{10}H_{14}$	(4)
1-methylnaphthalene	[90-12-0]	$C_{11}H_{10}$	(5)
9-methylphenanthrene	[883-20-5]	$C_{15}H_{12}$	(6)
Sulfur compounds			
propyl mercaptan	[107-03-9]	C_3H_8S	(7)
methyl propyl sulfide	[3877-15-4]	$C_4H_{10}S$	(8)
dibenzothiophene	[132-65-0]	$C_{12}H_8S$	(9)
Oxygen compounds			
phenol	[108-95-2]	C_6H_6O	(10)
2-phenanthrene carboxylic acid	[40452-20-8]	$C_{15}H_{10}O_2$	(11)
cyclohexyl carboxylic acid	[98-89-5]	$C_7H_{12}O_2$	(12)
Nitrogen compounds			
quinoline	[91-22-5]	C_9H_7N	(13)
carbazole	[86-74-8]	$C_{12}H_9N$	(14)
2(1*H*)-quinolinone	[59-31-4]	C_9H_7NO	(15)

[a] See Fig. 1.

Table 2. **Compounds Found in Petroleum Naphtha**[a]

Compound	CAS Registry	Molecular formula	Structure number
n-heptane	[142-82-5]	C_7H_{16}	(16)
2-methylheptane	[592-27-8]	C_8H_{18}	(17)
methylcyclopentane	[96-37-7]	C_6H_{12}	(18)
ethylcylohexane	[1678-91-7]	C_8H_{16}	(19)
1,3-dimethylbenzene (*m*-xylene)	[108-38-3]	C_8H_{10}	(20)
indan	[496-11-7]	C_9H_{10}	(21)
naphthalene	[91-20-3]	$C_{10}H_8$	(22)
tetrahydronaphthalene (tetralin)	[119-64-2]	$C_{10}H_{12}$	(23)
decahydronaphthalene (decalin)	[91-17-8]	$C_{10}H_{18}$	(24)
methyl mercaptan	[74-93-1]	CH_4S	(25)
3-methylthiacyclohexane	[5258-50-4]	$C_6H_{12}S$	(26)
3-(methylthio)pentane	[57093-84-2]	$C_6H_{14}S$	(27)

[a] See Fig. 5.

Table 3. **Compounds Found in Petroleum Middle-Distillates**[a]

Compound	CAS Registry Number	Molecular formula	Structure number
n-hexadecane (cetane)	[544-76-3]	$C_{16}H_{34}$	(28)
2-methylpentadecane	[1560-93-6]	$C_{16}H_{34}$	(29)
pristane (2,6,10,14-tetramethylhexadecane)	[1921-70-6]	$C_{19}H_{40}$	(30)
phytane (2,6,10,14-tetramethylhexadecane)	[638-36-8]	$C_{20}H_{42}$	(31)
pentamethyldecalin	[80655-44-3]	$C_{15}H_{28}$	(32)
fichtelite	[2221-95-6]	$C_{19}H_{34}$	(33)
adamantane	[281-23-2]	$C_{10}H_{16}$	(34)
biphenyl	[92-52-4]	$C_{12}H_{10}$	(35)
fluorene	[86-73-7]	$C_{13}H_{10}$	(36)
phenanthrene	[85-01-8]	$C_{14}H_{10}$	(37)
2-methylbenzothiophene	[1195-14-8]	C_9H_8S	(38)
dibenzothiophene	[132-65-0]	$C_{12}H_8S$	(39)
benzothiacyclohexane	[2054-35-5]	$C_9H_{10}S$	(40)

[a] See Fig. 6.

Table 4. **Fused-Ring Polynuclear Aromatic Hydrocarbons Found in Petroleum**[a]

Compound	CAS Registry Number	Molecular formula	Structure number
	cata-Condensed aromatics		
phenanthrene	[85-01-8]	$C_{14}H_{10}$	(**37**)[b]
chrysene	[218-01-9]	$C_{18}H_{12}$	(**8**)
picene	[213-46-7]	$C_{22}H_{14}$	(**42**)
	peri-Condensed aromatics		
fluoranthene	[206-44-0]	$C_{16}H_{10}$	(**43**)
pyrene	[129-00-0]	$C_{16}H_{10}$	(**44**)
benzo[α]pyrene	[50-32-8]	$C_{20}H_{12}$	(**45**)
benzoperylene	[11057-45-7]	$C_{24}H_{14}$	(**46**)
coronene	[191-07-1]	$C_{24}H_{12}$	(**47**)

[a] See Fig. 8.

[b] See Fig. 6.

Table 5. **Generalized Distillation Ranges for Products Obtained During Crude Oil Refining**

Product	Temperature range, °C	Carbon number range
gasoline	30–210	5–12
naphtha	100–200	8–12
kerosene and jet fuel	150–250	11–13
diesel and fuel oils	160–400	13–17
atmospheric gas oil	220–345	
heavy fuel oils	315–540	20–45
atmospheric residue	≥450	30+
vacuum residue	≥615	60+

Table 6. **International Oil Reserves as of December 31, 2003, 10^6 barrels**[a]

Rank[b]	Country	*Oil & Gas Journal*[c]	*World Oil*[d]
1	Saudia Arabia[e]	261,900[f]	259,400[f]
2	Iran[e]	125,800	105,000
3	Iraq[e]	115,000	115,000
4	Kuwait[e]	99,000[f]	99,375[f]
5	Canada[g]	178,893	4,957
6	United Arab Emirates[e]	97,800	66,230
7	Venezuela[e]	77,800	52,450
8	Russia	60,000	65,393
9	Libya[e]	36,000	30,500
10	Nigeria[e]	25,000	33,000
Top 10 total		*1,077,193*	*831,305*
11	United States	22,677	22,677
12	Qatar[e]	15,207	27,352
13	China	18,250	15,509
14	Mexico	15,674	14,597
15	Algeria[e]	11,314	14,000
16	Norway	10,447	9,395
17	Brazil	8,500	10,602
18	Kazakhstan	9,000	
19	Angola	5,412	8,800
20	Azerbaijan	7,000	
21	Oman	5,506	5,700
22	Indonesia[e]	4,700	5,500
23	Ecuador	4,630	4,950
24	India	5,371	4,002
25	United Kingdom	4,665	4,300
Top25 total		*1,225,546*	*978,689*
OPEC total		*869,521*	*807,807*
World total		*1,265,812*	*1,051,477*

[a] Ref. 94.

[b] Rank is based on an average of oil reserves reported in Refs. 95 and 96.

[c] Ref. 95.

[d] Ref. 96.

[e] Number of OPEC.

[f] Includes one-half of the reserves in the Neutral Zone.

[g] *Oil and Gas Journal* Canadian oil reserves include heavy (low gravity) oil.

Table 7. **Total U.S. Proved Reserves of Crude Oil ×10^6 barrels of 42 U.S. gal 1993–2003**[a]

Year	Adjustments (1)	Net revisions (2)	Revisions[b] and adjustments (3)	Net of sales[c] and acquisitions (4)	Extensions (5)	New field discoveries (6)	New reservoir discoveries in old fields (7)	Total discoveries (8)	Estimated Production (9)	Proved Reserves 12/31 (10)	Change from Prior Year (11)
1993	271	495	766	NA	356	319	110	785	2,339	22,957	−788
1994	189	1,007	1,196	NA	397	64	111	572	2,268	22,457	−500
1995	122	1,028	1,150	NA	500	114	343	957	2,213	22,351	−106
1996	175	737	912	NA	543	243	141	927	2,173	22,017	−334
1997	520	914	1,434	NA	477	637	119	1,233	2,138	22,546	+529
1998	−638	518	−120	NA	327	152	120	599	1,991	21,034	−1,512
1999	139	1,819	1958	NA	259	321	145	725	1,952	21,765	+731
2000	143	746	889	−20	766	276	249	1,291	1,880	22,045	+280
2001	−4	−158	−162	−87	866	1,407	292	2,565	1,915	22,446	+401
2002	416	720	1,316	24	492	300	154	946	1,875	22,677	+231
2003	163	94	257	−398	426	705	101	1,232	1,877	21,891	−786

[a] Ref. 97.

[b] Revisions and adjustments = Col. 1+ Col. 2.

[c] Net of sales and acquisitions = acquisitions – sales; NA = not available.

[d] Total discoveries = Col. 5 + Col. 6 + Col. 7.

[e] Proved reserves = Col. 10 from prior year + Col. 3+ Col. 4 + Col. 8 – Col. 9.

Notes: Old means discovered in a prior year. New means discovered during the report year. The production estimates in this table are based on data reported on Form EIA-23, "Annual Survey of Domestic Oil and Gas Reserve" and Form EIA-64A, "Annual Report of the Origin of Natural Gas Liquids Production." They may differ from the official EIA production data for crude oil, natural gas, and natural gas liquids for 2003 contained in the *Petroleum Supply Annual 2003*, DOE/EIA-0340(03) and the *Natural Gas Annual 2003*, DOE/EIA-0131(03).

Table 8. **U. S. Crude Oil Proved Reserves, Reserves Changes, and Production by States, ×10^6 barrels (42 U.S. gal) 2003**[a]

		Changes in reserves during 2003									
State and subdivision	Published proved reserves 12/31/02	Adjustments (+, −)	Revision increases (+)	Revisions decreases (−)	Sales (−)	Acquisitions (+)	Extensions (+)	New field discoveries (+)	New Reservoir discoveries in old fields (+)	Estimated production (−)	Proved reserves 12/31/03
Alaska	4,678	1	168	79	0	0	35	0	0	357	4,446
Lower 48 States	17,999	162	1,318	1,313	1,107	709	391	705	101	1,520	17,445
Alabama	51	1	4	0	0	0	2	0	0	6	52
Arkansas	49	9	2	1	4	2	0	0	0	7	50
California	3,633	−18	190	107	58	49	9	0	0	246	3,452
Colorado	214	−4	19	4	1	2	7	0	0	16	217
Florida	73	−1	0	1	0	0	0	0	0	3	68
Illinois	107	22	11	5	0	0	0	0	0	10	125
Indiana	15	5	1	0	0	0	0	0	0	2	19
Kansas	237	19	31	13	4	2	5	0	0	34	243
Kentucky	27[b]	2	2	4	0	0	0	0	0	2	25
Louisiana	501	3	57	75	46	38	31	0	6	63	452
Michigan	61	12	14	16	10	21	0	0	0	7	75
Mississippi	179	9	20	9	15	1	0	0	0	16	169
Montana	288	−6	15	8	2	5	42	0	0	19	315
Nebraska	18	0	1	0	0	0	0	0	0	3	16
New Mexico	710	−5	65	69	18	15	38	0	0	59	677
North Dakota	342	8	20	24	1	7	31	0	0	30	353
Ohio	67	9	4	8	1	0	0	0	0	5	66
Oklahoma	598	3	80	49	36	21	26	0	0	55	588
Pennsylvania	12[b]	−3	6	1	0	0	1	0	0	2	13
Texas	5,015	63	362	178	639	242	77	3	2	364	4,583
Utah	241	1	7	18	24	25	1	0	0	12	221
West Virginia	13[b]	0	2	1	0	0	0	0	0	1	13
Wyoming	524	24	29	36	23	36	5	0	0	42	517
Federal Offshore	5,009	8	376	686	225	243	115	702	93	515	5,120
Pacific (California)	565	1	10	2	0	0	22	0	0	30	566
Gulf of Mexico (Louisiana)	4,088	5	289	616	201	230	93	698	91	426	4,251

Table 8. (*Continued*)

		Changes in reserves during 2003									
State and subdivision	Published proved reserves 12/31/02	Adjustments (+, −)	Revision increases (+)	Revisions decreases (−)	Sales (−)	Acquisitions (+)	Extensions (+)	New field discoveries (+)	New Reservoir discoveries in old fields (+)	Estimated production (−)	Proved reserves 12/31/03
Gulf of Mexico (Texas)	356	2	77	68	24	13	0	4	2	59	303
Miscellaneous[c]	15	1	0	0	0	0	1	0	0	1	16
U.S. Total	*22,677*	*163*	*1,486*	*1,392*	*1,107*	*709*	*426*	*705*	*101*	*1,877*	*21,891*

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[a] Ref. 94.

[b] Indicates the estimate is associated with a sampling error (95 percent confidence interval) that exceeds 20 percent of the estimated value.

[c] Includes Arizona, Missouri, Nevada, New York, South Dakota, Tennessee, and Virginia.

Table 9. **International Petroleum Supply and Consumption Summary, × 10^6 barrels/day**[a]

		Projections								
		2010			2020			2025		
Supply and Consumption	2003	Low world oil price	Reference	High A world oil price	Low world oil price	Reference	High A world oil price	Low world oil price	Reference	High A world oil price
World oil price, 2003 $/barrel[b]	27.73	20.99	25.00	33.99	20.99	28.50	36.74	20.99	30.31	39.24
Production (conventional)[c]										
Industrialized countries										
U.S. (50 states)	9.09	9.55	9.61	9.95	8.86	9.21	9.76	8.36	8.82	9.60
Canada	2.25	1.82	1.83	1.91	1.58	1.60	1.70	1.54	1.57	1.68
Mexico	3.80	4.17	4.21	4.45	4.50	4.62	4.97	4.69	4.85	5.25
Western Europe[e]	6.69	6.32	6.35	6.65	5.44	5.51	5.85	4.92	5.00	5.35
Japan	0.13	0.08	0.08	0.09	0.06	0.06	0.09	0.05	0.06	0.09
Australia and New Zealand	0.66	0.95	0.96	1.01	0.86	0.89	0.95	0.83	0.86	0.93
Total industrialized	*22.62*	*22.89*	*23.05*	*24.06*	*21.30*	*21.89*	*23.32*	*20.40*	*21.16*	*22.90*
Eurasia										
former Soviet Union										
Russia	8.34	9.89	9.98	10.64	10.63	10.90	11.87	10.76	11.11	12.20
Caspian Area[e]	1.87	3.11	3.14	3.35	5.10	5.23	5.70	6.03	6.22	6.83
Eastern Europe[f]	0.22	0.33	0.33	0.35	0.40	0.41	0.44	0.44	0.45	0.48
Total Eurasia	*10.44*	*13.33*	*13.46*	*14.34*	*16.13*	*16.54*	*18.01*	*17.23*	*17.78*	*19.52*
Developing countries										
OPEC[g]										
Asia	1.38	1.57	1.47	1.19	1.78	1.51	1.14	1.88	1.56	1.16
Middle East	20.95	26.08	24.45	19.84	38.02	32.37	24.44	46.42	38.47	28.62
North Africa	2.99	3.67	3.44	2.79	5.21	4.44	3.35	5.77	4.78	3.56
West Africa	1.98	2.51	2.36	1.91	3.67	3.13	2.36	4.52	3.74	2.78
South America	2.85	3.56	3.34	2.71	5.21	4.44	3.35	6.27	5.20	3.87

Table 9. (*Continued*)

		Projections								
		2010			2020			2025		
Supply and Consumption	2003	Low world oil price	Reference	High A world oil price	Low world oil price	Reference	High A world oil price	Low world oil price	Reference	High A world oil price
Non-OPEC										
China	3.10	3.60	3.64	3.84	3.40	3.49	3.76	3.30	3.41	3.69
Other Asia	2.59	2.62	2.65	2.80	2.64	2.71	2.92	2.56	2.64	2.86
Middle East[h]	1.81	2.22	2.24	2.37	2.51	2.57	2.77	2.69	2.78	3.01
Africa	2.94	3.72	3.75	4.04	5.31	5.44	6.00	6.36	6.56	7.31
South and Central America	3.93	4.48	4.53	4.83	5.77	5.91	6.44	6.22	6.42	7.05
Total developing countries	*44.52*	*54.05*	*51.87*	*46.31*	*73.52*	*66.02*	*56.52*	*86.00*	*75.57*	*63.93*
Total production (conventional)	*77.58*	*90.26*	*88.38*	*84.72*	*110.95*	*104.45*	*97.85*	*123.53*	*114.51*	*106.34*
Production[i] (nonconventional)										
U.S. (50 states)	0.00	0.00	0.00	0.01	0.00	0.00	0.19	0.00	0.00	0.31
other North America	0.93	1.63	1.73	1.95	2.81	3.33	3.78	2.94	3.46	4.14
Western Europe	0.04	0.04	0.04	0.05	0.03	0.05	0.06	0.03	0.05	0.06
Asia	0.03	0.03	0.04	0.05	0.02	0.05	0.08	0.02	0.07	0.10
Middle East[h]	0.03	0.03	0.12	0.12	0.03	0.21	0.28	0.04	0.25	0.35
Africa	0.21	0.16	0.23	0.26	0.18	0.28	0.41	0.19	0.32	0.47
South and Central America	0.57	0.82	0.82	1.23	1.27	1.48	2.43	1.18	1.50	2.79
Total production (nonconventional)	*1.79*	*2.70*	*2.98*	*3.68*	*4.34*	*5.40*	*7.23*	*4.40*	*5.65*	*6.22*
Total production	*79.37*	*92.97*	*91.35*	*88.39*	*115.30*	*109.85*	*105.08*	*128.04*	*120.17*	*114.56*
Consumption[c]										
Industrialized countries										
U.S. (50 states)	20.00	23.23	22.98	22.41	27.34	26.32	25.47	29.55	27.93	26.85

U.S. Territories	0.36	0.40	0.38	0.35	0.48	0.43	0.39	0.54	0.47	0.42
Canada	2.17	2.39	2.30	2.15	2.68	2.62	2.39	3.16	2.80	2.55
Mexico	2.02	2.43	2.36	2.25	3.24	2.88	2.51	4.13	3.48	2.93
Western Europe[d]	14.22	15.00	14.72	14.22	16.15	15.45	14.82	16.60	15.71	15.06
Japan	5.58	5.91	5.70	5.34	6.46	5.69	4.95	6.93	5.84	4.99
Australia and New Zealand	1.04	1.29	1.27	1.23	1.60	1.54	1.49	1.77	1.69	1.63
Total industrialized	*45.38*	*50.66*	*49.72*	*47.95*	*58.15*	*54.93*	*52.01*	*62.68*	*57.92*	*54.44*
Eurasia										
Former Soviet Union	4.18	4.46	4.39	4.26	5.94	5.74	5.55	6.73	6.45	6.24
Eastern Europe[f]	1.42	1.58	1.56	1.53	1.93	1.89	1.85	2.15	2.09	2.05
Total Eurasia	*5.59*	*6.04*	*5.95*	*5.79*	*7.88*	*7.63*	*7.41*	*8.88*	*8.54*	*8.28*
Developing countries										
China	5.54	7.84	7.63	7.27	11.75	11.06	10.45	13.79	12.79	12.08
India	2.19	2.85	2.79	2.69	4.65	4.37	4.09	5.75	5.29	4.92
South Korea	2.17	2.57	2.51	2.39	2.96	2.75	2.56	3.21	2.93	2.72
Other Asia	5.74	7.37	7.28	7.11	9.76	9.47	9.20	11.07	10.66	10.35
Middle East[i]	5.58	6.90	6.83	6.73	8.49	8.34	8.21	9.28	9.08	8.93
Africa	2.72	3.16	3.13	3.07	4.26	4.13	3.99	4.85	4.66	4.49
South and Central America	4.69	5.89	5.81	5.69	7.68	7.48	7.30	8.89	8.61	8.40
Total developing countries	*28.64*	*36.57*	*35.98*	*34.94*	*49.55*	*47.59*	*45.80*	*56.83*	*54.01*	*51.90*
Total consumption	*79.60*	*93.27*	*91.65*	*88.68*	*115.57*	*110.14*	*105.22*	*128.39*	*120.47*	*114.62*
OPEC production[j]	30.60	38.04	35.79	29.48	54.88	47.21	36.75	65.79	55.13	42.44
non-OPEC production[j]	48.77	54.93	55.56	58.91	60.42	62.64	68.33	62.25	65.04	72.13
net Eurasia exports	4.84	7.29	7.51	8.55	8.26	8.92	10.60	8.35	9.25	11.23
OPEC market share	0.39	0.41	0.39	0.33	0.48	0.43	0.35	0.51	0.46	0.37

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[a] Ref. 98.

[b] Average refiner acquisition cost of imported crude oil.

[c] Includes production of crude oil (including lease condensates, natural gas plant liquids, other hydrogen and hydrocarbons for refinery feedstocks, alcohol and other sources.

[d] Western Europe = Austria, Belgium, Bosnia and Herzegovina, Croatia, Denmark, Finland, France, the unified Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Macedonia, Netherlands, Norway, Portugal, Slovenia, Spain, Sweden, Switzerland, United Kingdom, and Yugoslavia.

[e] Caspian area includes Other Former Soviet Union.

[f] Eastern Europe = Albania, Bulgaria, Czech Republic, Hungary, Poland, Romania, and Slovakia.

[g] OPEC = Organization of Petroleum Exporting Countries - Algeria, Indonesia, Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, the United Arab Emirates, and Venezuela.

[h] Non-OPEC Middle East includes Turkey.

[i] Includes liquids produced from energy crops, natural gas, coat, oil sands, and shale. Includes both OPEC and non-OPEC producers in the regional breakdown.

[j] Includes both conventional and non-conventional liquids production.

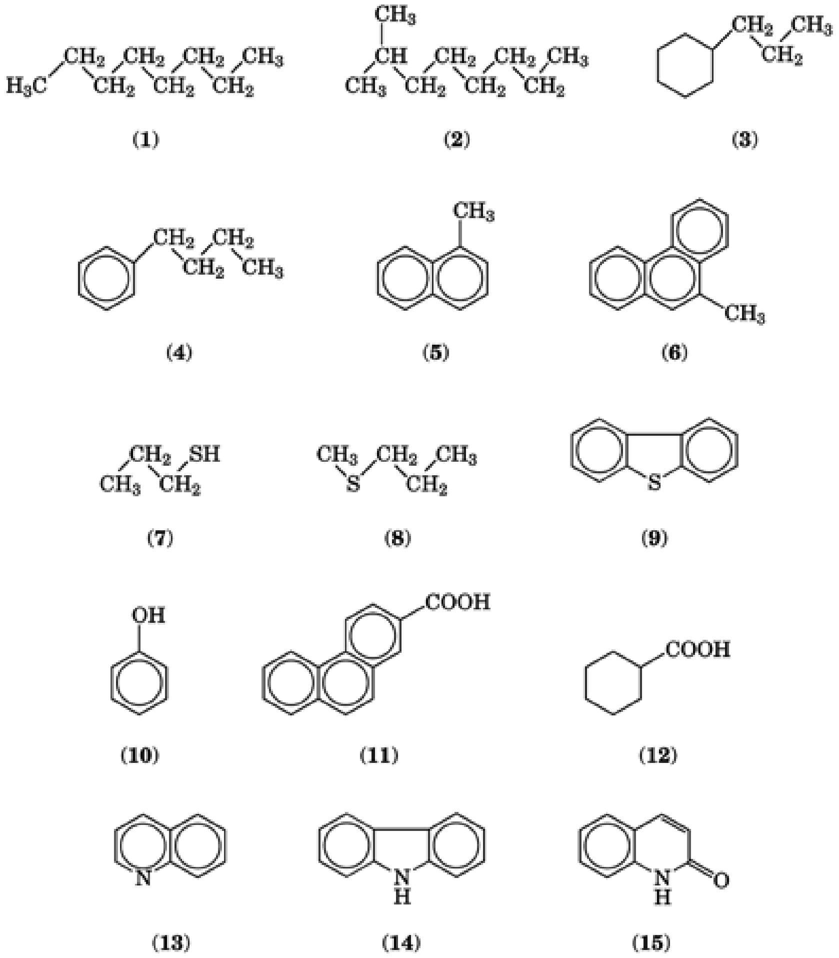
Table 10. **Estimated World Oil Resources, 1995-2025, $\times 10^9$ barrels**[a]

Region and country	Proved Reserves[b]	Reserve Growth[c]	Undiscovered[c]	Total
Industrialized				
United States	22.7	75.0	83.0	181.7
Canada	178.9	12.5	32.6	224.0
Mexico	15.7	25.6	45.8	87.1
Japan	0.1	0.1	0.3	0.5
Australia/New Zealand	3.6	2.7	5.9	12.1
Western Europe	18.2	19.3	34.6	72.1
Eurasia				
Former Soviet Union	78.0	137.7	170.8	386.5
Eastern Europe	1.4	1.5	1.4	4.2
China	18.3	19.6	14.6	52.5
Developing countries				
Central and South America	98.8	90.8	125.3	314.9
India	5.4	3.8	6.8	16.0
Other Developing Asia	11.0	14.6	23.9	49.5
Africa	87.0	73.5	124.7	285.2
Middle East	726.8	252.5	269.2	1,248.5
Total	*1.256.8*	*730.1*	*938.9*	*2,934.5*
OPEC	*869.5*	*395.6*	*400.5*	*1,665.6*
Non-OPEC	*396.3*	*334.5*	*538.4*	*1,269.2*

[a] Ref. 98.

[b] Ref. 95.

[c] Ref. 103.



(1) (2) (3)

(4) (5) (6)

(7) (8) (9)

(10) (11) (12)

(13) (14) (15)

Fig. 1. Structures of compounds in petroleum crude oils. See Table 1.

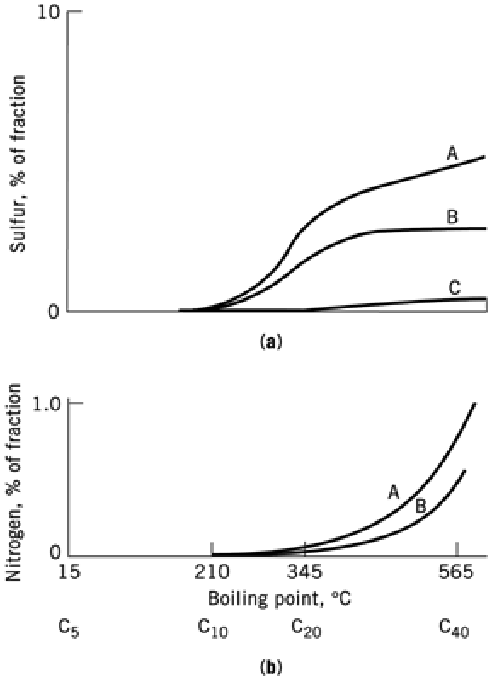


Fig. 2. Distribution of compounds as a function of crude oil boiling point: (**a**) sulfur where A, B, and C represent high (>2%), medium (ca 1.5%), and low (<0.1%) sulfur, respectively, and (**b**) nitrogen, where A and B represent high (ca 0.5%) and low (<0.1%) nitrogen, respectively.

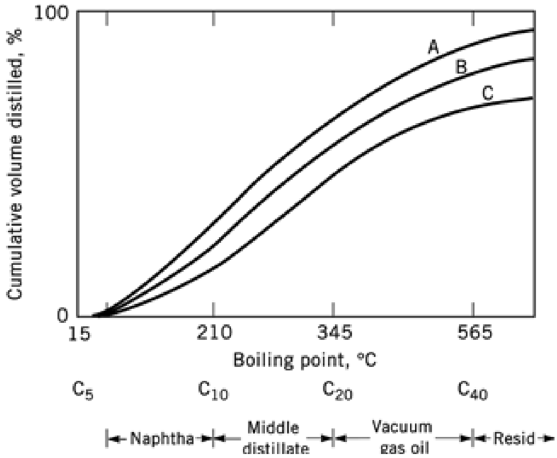


Fig. 3. Cumulative volume distilled as a function of boiling point from A, light; B, intermediate; and C, heavy crude oils (not including condensates).

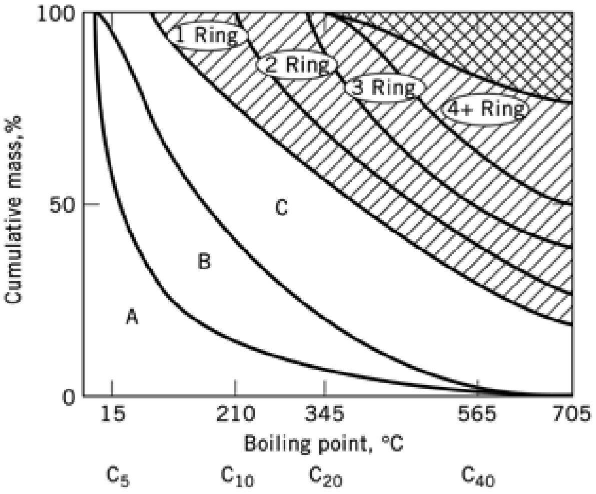


Fig. 4. Distribution of compound classes in crude oils as a function of boiling point. Region A represents normal paraffins; B, isoparaffins; C, naphthenes; □ the region of alkyl and napthenic aromatics; and ▨ the region of polars.

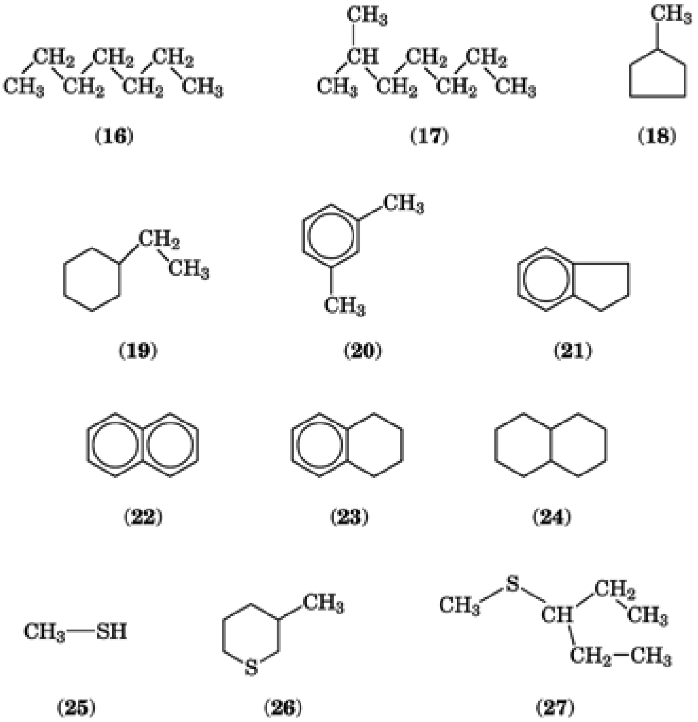
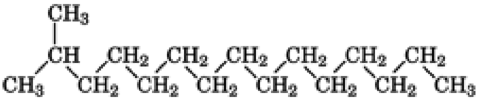


Fig. 5. Structures of compounds in petroleum naphtha. See Table 2.

(28)



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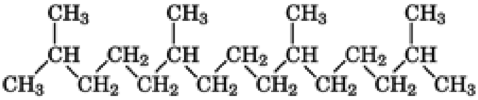

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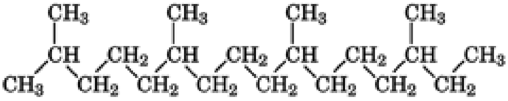

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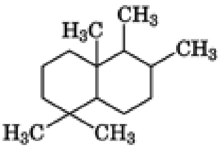

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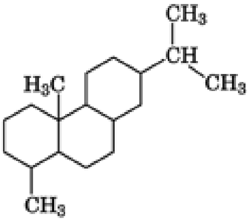

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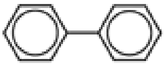

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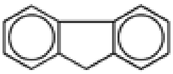

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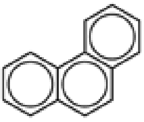

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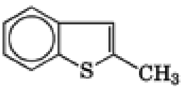

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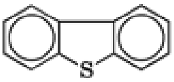

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Fig. 6. Structures of compounds in petroleum middle-distillates. See Table 3.

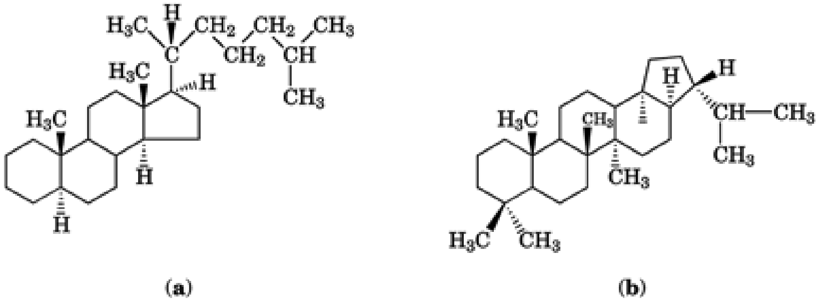
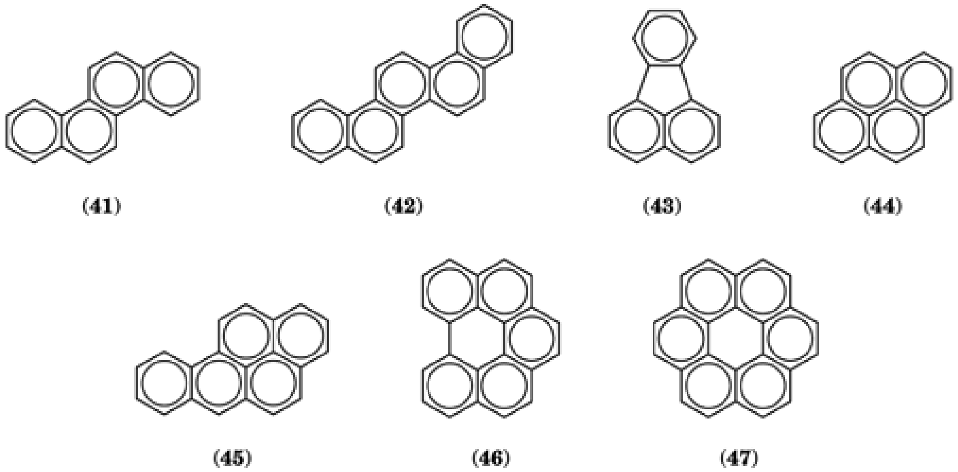


Fig. 7. Naphthenic biomarker compounds: (**a**) 5 α(*H*),14 α(*H*),17 α(*H*),20(*R*)-cholestane [481-21-0], a C_{27} sterane, and (**b**) 17 α(*H*),21 α(*H*)-hopane [13849-96-2], a C_{30} pentacyclic triterpane.



(41) (42) (43) (44)

(45) (46) (47)

Fig. 8. Structures of fused-ring polynuclear aromatic hydrocarbons. See Table 4.