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CHEMICAL TECHNOLOGY

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KIRK-OTHMER ENCYCLOPEDIA OF

CHEMICAL TECHNOLOGY

Fifth Edition

VOLUME 18

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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 and culminate permeable and eration, which the reservoir; sition of the p

A biogen not universal (1,2) and ther aspects (3). H the presence cycloalkanes Oils also conta characteristic compounds in The relative those in living alkanes (C₄) i dynamic equi leum with se low temperat few hundred range that ch composition of presence of p with a low te the material

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Compo crude oils. A what is thou matter in se dually incre mediate in

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 ($<^{\circ}\text{C}$) 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 influenced by available energy. An increase of 10°C results in a low molecular weight petroleum with biological characteristics. Therefore, at increasing depth of burial, the petroleum loses features such as alkanes, optical activity, and aromatics (11). These trends in petroleum generation process follow first-order kinetics (19) with variable values for the rate constant. More rigorous methods of determining reaction rates are more reliable.

An important example is the generation of methane. The bacteria produce methane (26), and have been found in Bacterially produced methane (BPM) in the Pee Dee Belemnite (PDB) and higher hydrocarbons in inorganic gases. Many of the giant Urengoy fields are thought to be bacterial. The gases are isotopically lighter than hydrocarbons. Examples are given.

Most petroleum generation occurs in and porosities, where the process of sorting and winnowing of materials. Reservoir rocks are commercially significant if they contain petroleum generated from the bitumen then the source rock contains the organic-rich source. Subsurface waters are involved in the generation process (31,32), and separate crude oil phases develop high intensity and the displacement of compaction and kerogen into adjacent permeable layers. The load (lithostatic) can be a factor in providing migration. The pressure gradient is expelled downward and top. The alkanes are eventually expelled. In c

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 $5.9 \times 10^{12} \text{ m}^3$ (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 deasphalting (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 degradation 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 gas in natural reservoirs is incorporated into sediments as organic methane; organic influence of increasing longer times; part of the subsequently migrates from reservoir; after the oil may be produced by degradation.

2. Composition

Petroleum, literally rock sent in source rocks as CARBON C1-C6). Petroleum (crude oil), and solid oil (see COAL; GAS, NATURAL) portion of petroleum discussed in this section. Properties. These properties such as boiling points, relative density (or specific gravity), and refractive index, more aromatic, and used to distinguish between oils.

The distribution of carbon skeletons of biological set of fingerprints for oil reservoir for exploration source input (marine, tional environment (clastic (water washing, biodegradation).

Knowledge of the conversion of raw petroleum was distilled and sold as gasoline (see LUBRICATION AND GASOLINE AND OTHER MOTOR FUEL (see AVIATION AND ASPHALTS, or it is converted into FEEDSTOCKS) such as ethylene, isoprene. Modern refining and hydrogen (qv). Cracking to break

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 HYDROCARBON 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.

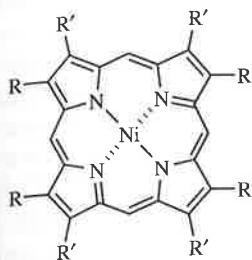
The distribution of biomarker isomers, molecules that retain the basic carbon skeletons of biological compounds from living organisms, serves not only as a set of fingerprints for oil-oil and oil-source correlation (to relate the source and reservoir for exploration), but also to give geochemical information 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

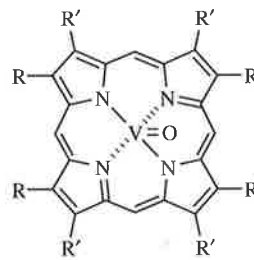
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of analytical techniques.



(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 $>500 \times 10^6 \text{ bbl}$ ($79.5 \times 10^6 \text{ m}^3$) of recoverable oil ($>100 \times 10^6 \text{ bbl}$ ($15.9 \times 10^6 \text{ m}^3$) 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 ($^\circ\text{API}$) 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 $35\text{--}40^\circ$ 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 ($1000 \text{ ft}^3 = 1 \text{ Mcf} = 28.3 \text{ m}^3$). Reserves of a trillion cubic feet (Tcf) ($28.3 \times 10^{12} \text{ m}^3$) 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 $4 \text{ L}/100 \text{ m}^3$ of natural gas liquids ($>0.3 \text{ gal}/1000 \text{ ft}^3$). 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 ($6000 \text{ ft}^3 = 1 \text{ bbl}$) 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 NSO's), 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

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+

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 asphaltene 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 residue, 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 FEEDSTOCKS, 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