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Paul R. Robinson

Petroleum Science and Technology

Upstream/Midstream

Second Edition

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Foreword

For sources of energy, people are transitioning from fossil resources, such as coal, oil and gas. We are relying more and more on renewables—electricity from solar, wind, nuclear, geothermal and hydroelectric—and liquid fuels and chemicals from biomass. This ongoing transition will last a long time, probably decades. At present, concern about climate change is the main driver for moving away from hydrocarbon-based energy in the past, we were worried about running out of oil. But due to advancements in technology for finding and producing oil and gas, experts are now estimating that known reserves will exceed 100 years, even after accounting for global economic growth.[1]

Meanwhile, during this transition, our usage of fossil fuels must be as clean and efficient as possible.

To accomplish this goal, we must understand oil & gas technology. That's why we wrote these books. The two volumes (Volume 1: Upstream/Midstream and Volume 2: Downstream) provide information for students who are considering a career in the oil/gas and chemical industries. They also are superb references for industry/academic/government professionals who want to see how this information fits with their particular endeavors.

The use of renewable biomass for fuels and chemicals is mentioned too, because it employs many of the techniques discussed in this book. For production of renewable diesel and sustainable aviation fuel (SAF) from plant-derived biomass and used cooking oil (UCO), adjustments must be made to handle large amounts of olefins, oxygen, and trace elements such as phosphorous and sodium. For recycling wastes, such as waste plastics and used motor oil, other precautions are needed.

The oil and gas industry abounds with opportunity. It is complex, a puzzle in which each piece affects many others. All kinds of science and engineering are required. The sciences include physics, geology, chemistry, biology, mathematics and genetics. The engineering disciplines include chemical, mechanical, electrical,

[1] Daniel Yergin, *The Quest: Energy, Security, and the Remaking of the Modern World*, Penguin Randon House (2011)

environmental, and metallurgical. Important specializations include control, instrumentation and robotics. Some of the most sophisticated IT technology is employed, including augmented intelligence (AI).

Safety and protecting the environment are of utmost importance. In the books, examples of industry incidents provide important lessons, knowledge of which can prevent future incidents.

We hope these works will assist you not just now, but throughout your careers.

Contents

Chapter 1
Characteristics and Historical Events

1.1 What is Petroleum?

There are several ways to answer this question:

In appearance, petroleum is a naturally occurring liquid found beneath the Earth's surface. Petroleum liquid usually is associated with reservoir gas. Together they are known as crude oil and natural gas, or simply oil and gas. Some crude oils are as clear as vegetable oils. Others are green, brown, or black. Some flow freely like water. Others are viscous and don't flow at all unless they are heated. Some are solid and are recovered by mining. Tar sand, for example, is mined; it is a combination of clay, sand, water, and bitumen (heavy black viscous oil). These characteristics vary with location, depth, and age of the field.

The English word "petroleum" means "rock oil" or "oil from stone," which is derived from the Greek *pétra*, meaning "rock", and *oleum*, meaning "oil." In Chinese, the characters for petroleum are 石油, pronounced *shi-yóu* which also means "stone (rock) oil."

In composition, petroleum is a complex mixture of countless organic molecules derived from ancient living organisms. The molecules are mostly hydrocarbons, including small amounts of heteroatom-containing hydrocarbons, contaminated with various amounts of inorganic matter. The major heteroatoms are sulfur, nitrogen, oxygen, and trace metals.

Geologically, petroleum and natural gas are fossil hydrocarbons associated with certain geological formations, known as reservoirs or traps.

Economically and politically, crude oil is an important energy and material source. In 2020, it accounted for 35% of U.S. energy consumption, as shown in Fig. 1.1. Its close cousin, natural gas, accounted for 34%. In the figure, natural gas from shale

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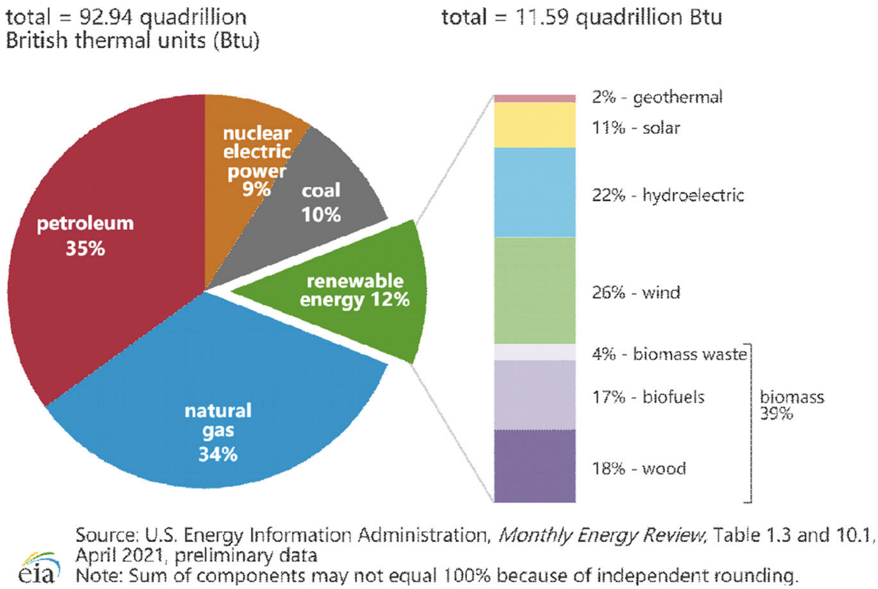

Fig. 1.1 U.S. Energy Consumption by *Source*—2020 [1]

is part of the coal/peat/shale slice of the pie. U.S. renewable energy use has been increasing: the figure shows that it reached 12% in 2020. In addition to serving as our primary source of liquid fuels, petroleum is a raw material from which we produce: solvents, lubricants, petrochemicals, construction materials, and thousands of consumer products.

The graphics in Fig. 1.2 show breakdowns of world energy consumption by source from 1995 to 2020. Units of measure are exajoules (EJ, 10^{18} J). Graphic A on the left-hand side shows how total consumption has been increasing in concert with world-wide population growth as well as accelerating economic development in Africa and (primarily) in Asia. Graphic B on the right-hand side shows the information as percentages. BP analysts say:

"Primary energy consumption rose by 1.3% last year, less than half its rate in 2018 (2.8%). Growth was driven by renewables (3.2 EJ) and natural gas (2.8 EJ), which together contributed three quarters of the increase. All fuels grew at a slower rate than their 10-year averages, apart from nuclear, with coal consumption falling for the fourth time in six years (−0.9 EJ). By region, consumption fell in North America, Europe and CIS (Commonwealth of Independent States, former Soviet Union) and growth was below average in South and Central America. In the other regions, growth was roughly in line with historical averages. China was the biggest individual driver of primary energy growth, accounting for more than three quarters of net global growth." Renewables include wind, hydro, solar, biomass, and geothermal.

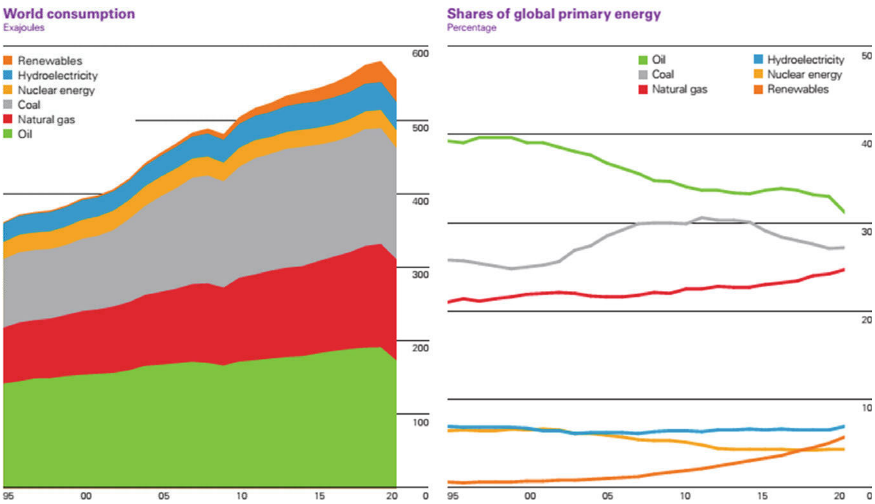

Fig. 1.2 World consumption of energy from 1995 to 2020. (From BP, page 11) [2]

Referring to Graphic B:

> Oil continues to hold the largest share of the energy mix (33.1%). Coal is the second largest fuel but lost share in 2019 to account for 27.0%, its lowest level since 2003. The share of both natural gas and renewables rose to record highs of 24.2% and 5.0% respectively. Renewables have now overtaken nuclear, which makes up only 4.3% of the energy mix. The share of hydroelectricity has been stable at around 6% for several years.

The fall in coal is due mainly to decreases in the United States and in China, which are the world's largest consumers. The decrease in China is being driven by a concerted recent effort to improve air quality and decrease CO_2 emissions. Natural gas has been rising in part due to increased production with fracking technology in the United States, where natural gas and renewables are rapidly displacing coal. Renewables have been increasing at an astounding rate in the United States, where in 2020 they accounted for 12% (see Fig. 1.1). Nuclear energy remains significant in certain countries, including the United States and France.

Figure 1.3 compares regional consumption patterns for 2019. According to BP analysts:

> "Oil remains the dominant fuel in Africa, Europe, and the Americas, while natural gas dominates in CIS and the Middle East, accounting for more than half of the energy mix in both regions. Coal is the dominant fuel in the Asia Pacific region. In 2019 coal's share of primary energy fell to its lowest level in our data series in North America and Europe."

Renewables are largest in Europe, due to climate change legislation, and in Brazil, where ethanol from sugar cane is considerable. Renewables are accelerating at a breathtaking rate in the United States. Recent announcements indicate that the trend is likely to continue. For example, in August 2020, Phillips 66 announced that its refinery in Rodeo, California, will be converted into the world's largest renewable

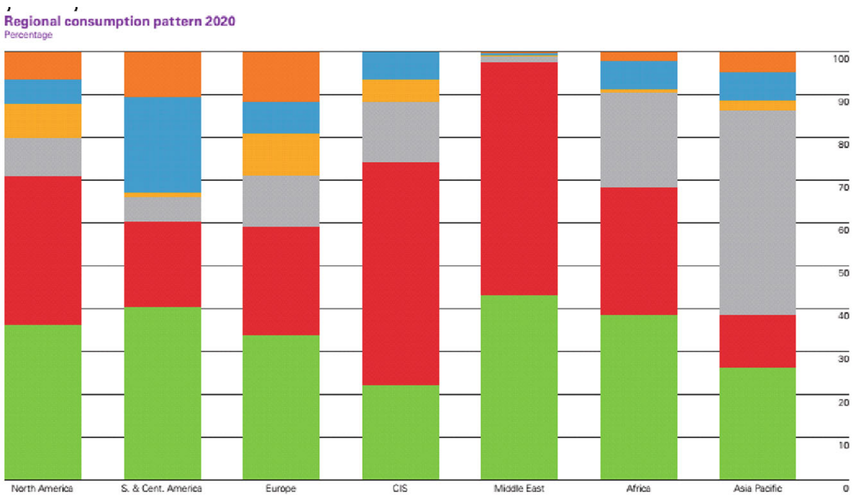

Fig. 1.3 Regional energy consumption pattern in 2020. Color codes referred to Fig. 1.2. (From BP, page 11) [2]

fuels plant [3]. In October 2020, Marathon Petroleum applied for permits to convert its refinery in Martinez, California into a renewable diesel facility producing about 17.5 million barrels per year of renewable fuels, primarily diesel, from bio-based feedstocks such as animal fats, soybean oil, and corn oil [4].

Figure 1.4 shows that fossil fuels still account for more than 62% of the world's electricity generation. Of this, only a small amount (3.1%) comes from petroleum. The major non-fossil sources are hydroelectric (15.6%) and nuclear (10.4%). For electricity generation in the United States during 2020, renewables (20%) surpassed coal (19%) as the second largest primary source, after natural gas (40%) [5].

1.2 Fossil Hydrocarbons (Fossil Fuels)

When discussing petroleum, it is useful to introduce other fossil hydrocarbons. These valuable resources appear in many forms which are described below.

1.2.1 Natural Gas

Natural gas in reservoirs contains mostly methane (CH_4). Like crude oil, the origin of natural gas is biological, and oil and gas are formed by the same natural forces. Hence, most (but not all) petroleum reservoirs contain both oil and gas. As ancient biomass is transformed into fossil hydrocarbons, different oil- and gas-generation

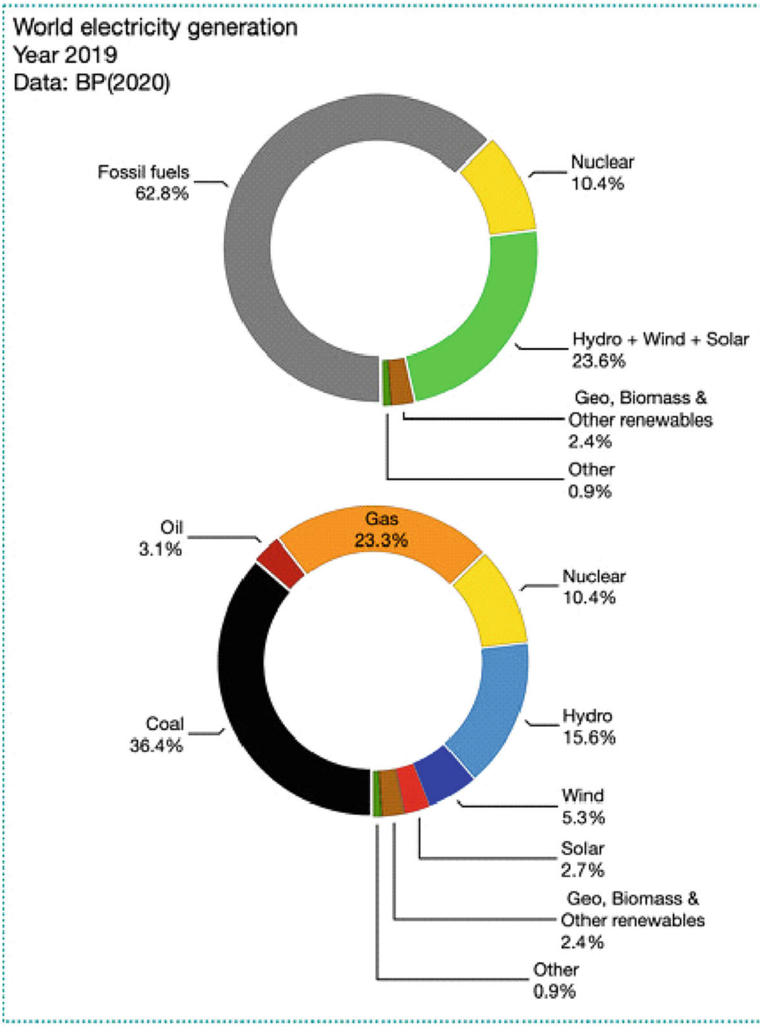

Fig. 1.4 World electricity generation by source in 2019. (Based on data from BP, pp. 60–61). [2] "Hydro" = hydroelectric, "Geo" = geothermal

windows correspond to different residence times at different depths, pressures, and temperatures. Natural gas is formed when liquid petroleum is "over-matured" due to excess thermal stress in deep formations.

Methane can also be formed from anaerobic digestion in natural wetlands, rice paddies, emissions from livestock, organic wastes in landfills as biogenic methane. Methane is formed due to incomplete combustion of biomass in forest fires, charcoal burning, etc. The radioactive carbon isotope, ^{14}C, is present in recent biogenic methane but absent in natural gas from fossil sources. This is because ^{14}C has a half-life of 5,700 years, so in hydrocarbon deposits that are millions of years old, it is completely absent.

Natural gas that contains almost nothing but methane, with only traces of other compounds, is *dry gas*. When people talk about natural gas for heating and electrical power generation, they are commonly referring to dry gas. If natural gas contains significant amounts of ethane, propane, butanes, and higher hydrocarbons, it is called *wet gas*.

Natural gas that contains almost nothing but methane, with only traces of other compounds, is *dry gas*. Dry natural gas can also be called as consumer-grade natural gas. When people talk about natural gas for heating and electrical power generation, they are commonly referring to dry gas. If natural gas contains significant amounts of ethane, propane, butanes, and higher hydrocarbons, it is called *wet gas*. The heavier components can be recovered individually or as condensate or natural gas liquid (NGL) in natural gas processing plants. *Natural gasoline* is a condensate fraction that mostly consists of pentane. *Sour gas* contains hydrogen sulfide, and *acid gas* contains carbon dioxide and/or hydrogen sulfide. Sour-gas processing plants coproduce elemental sulfur, which is used to make sulfuric acid and fertilizers. Some natural gas contains commercial quantities of noble gases—helium (the product of α-decay in radioactive minerals underground), neon and/or argon. Almost all commercial helium comes from natural gas plants [6].

Geochemists favoring biogenic origins for petroleum from overwhelming evidence do not deny the existence of abiogenic hydrocarbons [7]. The presence of methane on Saturn's moon Titan and in the atmospheres of Jupiter, Saturn, Uranus, and Neptune is cited as evidence of the formation of hydrocarbons without biological origins.

1.2.1.1 Unconventional Gas

Unconventional gas refers to natural gas that cannot be recovered by conventional techniques. Instead, it is obtained from non-conventional sources such as coal-bed methane and tight shale [8]. Its extraction requires special or advanced production methods, such as a combination of horizontal drilling and hydraulic fracturing. However, independent uses of horizontal drilling and hydraulic fracturing are no longer considered unconventional because they are widely used in common practice. Even though combining the two in a certain way can be considered conventional, the shale gas and tight gas are considered unconventional because they are trapped source rocks rather than in reservoirs through migration/accumulation. Unconventional gas includes shale gas, tight gas, coal bed methane, and methane hydrates.

Shale Gas

Unlike conventional gas, which resides in highly porous and permeable reservoirs and can be tapped by standard wells, shale gas remains trapped in its original source rock formed from the sedimentary deposition of mud, silt, clay, and organic matter on the floors of shallow strata. Like shale oil, shale gas can be recovered economically by hydraulic fracturing, which will be discussed in Chap. 7.

Tight Gas

Tight gas refers to natural gas that is trapped in reservoirs with poor permeability and porosity. It is extremely difficult or impossible for the gas to move through such strata into a standard well. These types of reservoirs commonly require a combination of horizontal drilling and hydraulic fracturing to economically extract gas and oil.

Coal Bed Methane

Coal Bed Methane (CBM) is a type of unconventional natural gas found in coal deposits or coal seams. Essentially, the term refers to methane adsorbed into the solid matrix of the coal. CBM is formed during the process of coalification, the transformation of plant material into coal. Here, coal is both the source rock and reservoir simultaneously; there is no obvious trap definition. Unlike the natural gas from oil and gas reservoirs, it is called “sweet gas” because of its lack of hydrogen sulfide. It contains very little heavier hydrocarbons such as propane, butane, and condensate. It often contains up to a few percent carbon dioxide. In recent decades it has become an important source of energy in United States, Canada, China, Australia, and other countries.

CBM was first removed from coal mines by ventilation as a safety measure to reduce explosion hazards posed by methane gas in the mines. In modern times, it is recovered from underground coal before, during, or after mining operations. CBM can also be extracted from inaccessible coal seams that are relatively deep, thin or of poor or inconsistent quality. Vertical and horizontal wells are used to develop CBM resources. Coal seams are typically saturated with water. Consequently, the coal must be dewatered for efficient gas production by reducing the hydrostatic pressure and releasing absorbed (and free) gas out of the coal.

Coalbed methane deposits have also attracted interest for their potential for carbon sequestration. Injecting carbon dioxide (CO_2) into hard-to-mine coal seams causes the CO_2 to displace the methane locked within the coal, enhancing the recovery of the natural gas resource while storing the CO_2 where it will not contribute to global warming.

Methane Hydrate (Clathrate)

Methane is also present in another form as methane hydrate (clathrate) [9] where a fixed quantity of methane is incarcerated in a cluster of water molecules as an ice-like crystal. Vast amounts of methane hydrate deposits occur on the deep ocean floor, on continental margins, and in places north of Arctic Circle. It is estimated that methane hydrate deposits contain around 6.4 trillion (6.4×10^{12}) tonnes of methane [10]—twice as much carbon as all other fossil fuels on earth. However, the necessary technology for industrial production of the methane hydrate is not yet available. Hydrocarbon clathrates cause problems for the petroleum industry because they can form inside gas pipelines, often resulting in obstructions.

The production of methane hydrate is fundamentally different than the extraction of oil and natural gas. Conventional recovery is based on hydrocarbons flowing naturally through the pores of reservoirs to the production well. Hydrates, on the other hand, are solid. The ice crystals must be dissociated before methane can be extracted. Several methods have been tested, such as hot water injection to break down the hydrate and release methane, depressurization by drilling into the deposits to release methane, and carbon dioxide injection to replace methane in the clathrate molecular cage.

Carbon dioxide hydrates are more stable than methane hydrates. Carbon dioxide captured from natural gas and coal power plants and injected into hydrates for storage is a strategy of carbon dioxide sequestration, which reduces its emission into the atmosphere. Each technique has its challenges and limitations. Hence, it is still uncertain which of these methods will be best suited for production at industrial scales.

Future global warming has the potential to destabilize the methane clathrates found on continental margins and permafrost regions, resulting in the release of methane gas into the atmosphere worldwide. [11] This could produce a catastrophic positive feedback loop: increasing the temperature of permafrost and ocean water releases additional methane into the atmosphere, further increasing air and ocean temperatures, which further increases methane release from hydrates and permafrost melting, and so on.

As a a greenhouse gas, methane is more than 28 times as bad as carbon dioxide. One source says that over the first 20 years after it reaches the atmosphere, it is more than 80 times worse [12]. Fig. 1.5 displays the global distribution of methane hydrates, known and inferred [13].

1.2.2 Liquids (Crude Oils)

Crude oil is the common name for liquid petroleum. Crudes are complex mixtures. There are about 300 openly traded "named crudes" with significantly different compositions. Crudes typically are named for their source country, reservoir, and/or some distinguishing physical or chemical property. Table 1.1 presents the selected physical and chemical properties for 10 crude oils.

The lightest liquid is *condensate*, also known as natural gas liquids (NGL), with boiling points in the light gasoline range. *Light crude oils* have low boiling points, low densities (specific gravities), low viscosities, low sulfur, and low or negligible amounts of nitrogen and other hetero-atom compounds. In sweet crudes such as Tapis (a Malaysian crude), the sulfur content is unusually low (0.028%). Sour crudes

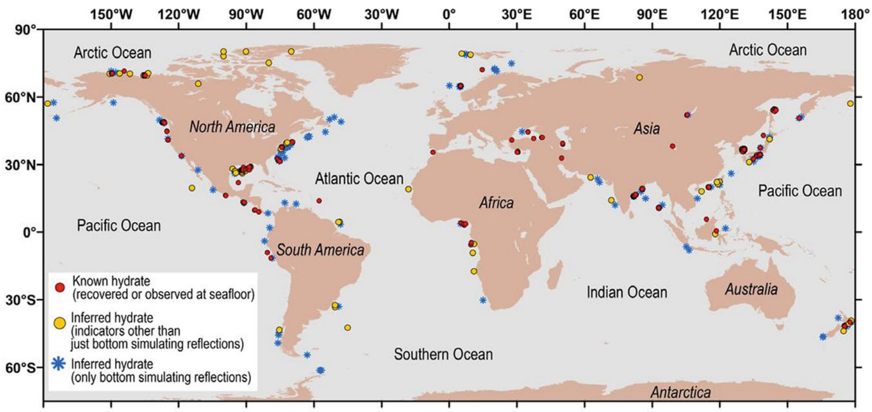

Fig. 1.5 Global distribution of methane hydrates, known and inferred [13]

Table 1.1 Selected properties of 10 crude oils [14]

Crude oil	API gravity[a]	Residue[b] (vol%)	Sulfur (wt%)	Nitrogen (wt%)
Alaska North slope	27.1	53.7	1.2	0.2
Arabian light	33.8	54.2	1.8	0.07
Arabian heavy	28.0	46.6	2.8	0.15
Athabasca	8	50.8[c]	4.8	0.4
Brent (North Sea)	39	38.9	0.3	0.10
Boscan (Venezuela)	10.2	82.8	5.5	0.65
Kuwait	31.4	49.5	2.3	0.14
Shengli (China)	24.7	72.5	0.8	0.41
Tapis Blend (Malaysia)	45.9	26.3	0.028	0.018
West Texas	40.2	36.4	0.3	0.08

[a]*API Gravity* is related to specific gravity by the formula: API = (141.5/(specific gravity @ 60 °F))–131.5
[b]Unless otherwise stated, cut point = 343 °C-plus (650 °F-plus) for atmospheric resides
[c]Cutpoint = 525 °C (913 °F) for vacuum resides, extra-heavy crude oils and bitumen

have more sulfur, which gives them a tart taste. The commonly accepted dividing line between sweet and sour crudes is 0.5 wt%. Synthetic crude oil is produced from coal, kerogen, or natural bitumen. Processing costs are higher for conventional or synthetic crudes with high density and large amounts of sulfur, nitrogen, and trace contaminants. Shengli and many other Chinese crudes are very high in nitrogen, which can present special challenges during processing, especially when the nitrogen content is similar to or greater than the sulfur content.

Heavy crude oils possess high density—close to that of water. *Extra-Heavy oils* have densities greater than water. Both have very high boiling points and

Table 1.2 Distillation yields for four selected crude oils [14]

Source field	Brent	Bonny light	Green canyon	Ratawi
Country	Norway	Nigeria	USA	Middle East
API gravity	38.3	35.4	30.1	24.6
Specific gravity	0.8333	0.8478	0.8752	0.9065
Sulfur, wt%	0.37	0.14	2.00	3.90
Yields, wt% feed				
Light ends	2.3	1.5	1.5	1.1
Light naphtha	6.3	3.9	2.8	2.8
Medium naphtha	14.4	14.4	8.5	8.0
Heavy naphtha	9.4	9.4	5.6	5.0
Kerosene	9.9	12.5	8.5	7.4
Atmospheric gas oil	15.1	21.6	14.1	10.6
Light VGO	17.6	20.7	18.3	17.2
Heavy VGO	12.7	10.5	14.6	15.0
Vacuum residue	12.3	5.5	26.1	32.9
Total naphtha	30.1	27.7	16.9	15.8
Total middle distillate	25.0	34.1	22.6	18.0
Naphtha plus distillate	55.1	61.8	39.5	33.8

high viscosities (>1000 centipoise (cP)). They also contain high concentrations of heteroatom-atom-containing hydrocarbons.

Distillation yields are an exceptionally important property of petroleum because the yields determine the value of crude oil. Crudes containing larger amounts of light, low-boiling fractions—naphtha, kerosene/jet fuel, and gas oil (diesel)—are more valuable. Table 1.2 shows distillation data for four common crudes. The naphtha content of Brent is twice as high as Ratawi, and its vacuum residue content is 60% lower. Bonny Light crude yields the most middle distillate and the least amount of vacuum residue.

1.2.2.1 Unconventional Oil

As with unconventional gas, unconventional oil refers to oil for which the recovery requires unconventional methods. These include oil from oil shale (tight oil), where the shale must be hydraulically fractured to free the oil. Oil from tight shale tends to be lighter and easier to process than most conventional crudes; examples include Eagle Ford crude from Texas and Bakken crude from South Dakota. Other unconventional oils contain hydrocarbons that not only require special recovery techniques but also need additional processing and refining to convert them into traditional petroleum products. Heavy unconventional oil includes bitumen from oil sands, oil that is thermally recovered from shale, and other heavy- and extra-heavy oils. Heavy unconventional oils do not flow near the surface and sometimes do not flow at all unless heated; they are in a solid or near-solid state.

1.2.3 Bitumen, Asphalt, Tar

Colloquially, the terms “bitumen,” “asphalt,” and “tar” are used interchangeably to describe certain black, viscous, semi-solid mixtures of hydrocarbons. Geologists say “bitumen” when referring to natural deposits, such as the famous La Brea Tar Pits. In the United States, bitumen produced by crude oil refining is called “asphalt”. Outside the United States, bitumen from refineries is called “refined bitumen” or simply “bitumen.” Oil that is severely degraded by weathering and biodegradation, along with the oil on oil sand or tar sand, is also called “bitumen”.

“Pitch” is a synonym for bitumen. “Pitch” is also used to describe refractory fractions from certain residue upgrading processes.

Like extra-heavy oils, natural bitumens have specific gravities greater than 1.0 (API gravity <10), but the viscosities are higher (>10,000 cP). Under ambient conditions, natural bitumen is a soft and/or sticky solid, but when heated it flows. In practical terms, it is recovered as a solid but transported and processed as a liquid by adding diluents to lower viscosity. It is important to distinguish between natural bitumen and refined bitumens. The latter are specialty products with rather tight specifications. Refined bitumen is used primarily for paving and construction (roofing). Tar sands (also known as oil sands) contain much of the world’s recoverable bitumen.

1.2.4 Oil Reserves

In 2022, the largest oil reserves were in Venezuela. These reserves totaled 303 billion barrels, most of which are extra-heavy oils deep underground or offshore. Saudi Arabia was in second place with proven reserves of 267 billion barrels, mostly conventional and near the surface. Canada was in third place, where the proven reserves are 167 billion barrels, mostly as bitumen in oil sands; in addition, the province of Alberta holds 1.4 billion barrels of conventional crude [15]. In comparison, for that same year, proven reserves of conventional crude oil in Middle East were about 800 billion barrels, where Iran ranked fourth at 155 billion barrels and Iraq fifth at 145 billion barrels [16]. In tar sands (oil sands), bitumen is associated with sand and clay, from which it can be recovered with hot water or steam. Venezuela’s oil sands are technically “extra-heavy oil” deposits since they don’t contain material with viscosity greater than 10,000 centipoise (cP). The viscosities of Canadian tar sands vary widely, ranging from 10,000 to 600,000 cP, while those of Venezuelan tar sands are more uniform, typically ranging from 4,000 to 5,000 cP. [17] The specific gravities of both extra-heavy oil and bitumen are greater than 1, which is the specific gravity of water. (A specific gravity of 1 is equivalent to an API gravity of 10). In the United States, tar sands are found primarily in Eastern Utah, mostly on public lands. These deposits contain 12–19 billion barrels of recoverable oil. Tar sand oils require unconventional techniques for recovery.

1.2.5 Solids

Kerogen is the solid organic matter in sedimentary rocks. Unlike bitumen, it does not flow even when heated. But at high-enough temperatures—e.g., 900 °F (480 °C)—it decomposes into gases, liquids, bitumen, and refractory coke. Huge amounts of kerogen are trapped in oil shale deposits for which hydraulic fracturing is ineffective. Fenton et al. [18] estimated that 1.3 trillion barrels of kerogen worldwide could be recovered and converted into hydrocarbon gases and liquids.

Methods for producing fluids from kerogen include direct retorting, in which shale is mined and heated with process gas, and oxidative retorting, in which heat is generated from in situ combustion supported by air that is pumped into the formation through tunnels.

Table 1.3 presents composition information on Green River oil shale from the western United States. About 91% of the kerogen is hydrogen and carbon, but only 15% of the shale is kerogen. Shale oil—synthetic crude from the kerogen in oil shale—tends to contain high amounts of arsenic, a severe poison for refinery catalysts. Some contain mercury, which also poisons catalysts and can contaminate petroleum products. Usually, the arsenic is removed in existing hydrotreating units with special high-nickel chemisorption catalysts, which trap the arsenic by forming nickel arsenides. Other petroleum solids or semisolids include asphaltenes, wax, and gas hydrates, which can block pipelines and/or drill pipes and interfere with the flows of oil and gas.

Coal is another non-petroleum hydrocarbon resource. It is a black or brown combustible rock composed mostly of carbon, hydrocarbons, and ash. Generally,

Table 1.3 Typical composition of green river oil shale

Kerogen content: 15 wt %[a]	
Kerogen composition, wt% of kerogen	
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1
Oxygen	5.8
Total	100
Minerals, wt% of mineral content	
Carbonates	48
Feldspars	21
Quartz	15
Clays	13
Analcite and pyrite	3
Total	100

[a] Equivalent to 25 gallons oil per ton of rock

it is classified into four ranks—anthracite, bituminous, sub-bituminous, and lignite. Anthracite is relatively rare, containing 86–97% carbon, and it has a high heating value. Bituminous coal is far more common. It contains 45–86% carbon and is burned to generate electricity. It is also used extensively in the steel and iron industries. Sub-bituminous coal contains 35–45% carbon, and lignite contains 25–35% carbon. Lignite is crumbly, has high moisture content and relatively low heating value. In regions such as China, where coal is abundant but oil is scarce, coal is converted into liquids, both directly and indirectly. Direct processes convert coal into various combinations of coal tar, oil, water vapor, gases, and char. The coal tar and oil can be refined into high-quality liquid fuels [19].

Compared to liquids and gases, solids are harder to recover, transport, and refine. Liquids and gases can be pumped through pipelines and into refineries with relative ease. Slurries of coal and water can be transported as fluids, but at the destination, the water must be removed, and the coal must be purified at considerable expense before it can be burned or gasified. Solid coal is consumed on a large scale to produce heat, steam, and electricity. These days, coal-powered transportation vehicles are almost non-existent. Coal-burning steam ships and railway locomotives are less efficient than their oil-powered counterparts. Typically, the specific energy of a ton of fuel oil from petroleum is 90% greater than a ton of bituminous coal and 40% greater than a ton of anthracite. Even if for some reason a railroad or shipping company wanted to burn coal, doing so wouldn't be practical due to the present lack of coaling stations. Coal is widely used for generating electricity in many countries, including China, India, and the United States. In China and the United States, coal is being supplanted by natural gas and renewables—primarily wind and solar energy.

Sulfur, ash, and trace metals in coal cause severe contamination of air with sulfur, mercury, and particulates. Upon combustion, the sulfur becomes sulfur oxides (SOx), primarily SO_2. High-temperature combustion generates nitrogen oxides (NOx) from the nitrogen and oxygen in air. Smog (photochemical smog) is generated by sunlight-induced reactions between NOx and volatile organic hydrocarbons (VOC); reaction products include ground-level ozone, an especially noxious pollutant. Sulfate particulates, ranging in size from 1 to 20 microns, can be carried by winds hundreds of miles, eventually returning to the earth as dry or wet "acid deposition." Wet deposition is commonly called "acid rain," which also can contain NOx. The combination of smog, particulates, and acid rain can be deadly, especially in large cities without adequate ventilation.

Coal mining and combustion are predominant causes of mercury pollution. Mercury enters ecosystems in many ways. High concentrations of mercury in salmon, tuna, and other marine top predators begin with the production of methyl mercury by microorganisms, followed by consumption of those organisms by small fish, which are then consumed by larger fish, etc.

Developed in 1925, the Fischer-Tropsch (F-T) process is the main indirect route for converting coal into liquids. The coal is first gasified to make synthesis gas (syngas)—a balanced mixture of CO and hydrogen. Over F-T catalysts, syngas is converted into a full range of hydrocarbon products, including paraffins, alcohols, naphtha, gas oils, and synthetic crude oil. The F-T process was used extensively in

Germany between 1934 and 1945. In South Africa, the F-T process was used on a large scale to manufacture chemicals and fuels due to embargos during apartheid. Today, F-T is a leading candidate for converting waste plastic into chemicals.

Synthesis gas is also derived from natural gas via steam-methane reforming (SMR). It can be converted into hydrogen and petrochemicals such as methanol. Worldwide, vast amounts of hydrogen are used to produce ammonia via the Haber–Bosch process.

1.3 Use of Petroleum: A History

Examination of artifacts shows that humans were using petroleum long before writing emerged as a means of recording events and conveying knowledge from one generation to the next [20]. According to archaeologists, bitumen was used for hafting spears as early as 70,000 BCE near Umm el Tlel, in present-day Syria [21]. Neanderthals used bitumen, too. A paper by Cârciumaru, et al. provides evidence that Neanderthals in Romania also hafted spears with bitumen between 28,000 and 33,000 BCE; the dates are based on uncalibrated ^{14}C dating [22].

Jane McIntosh's excellent book [23] about the ancient Indus valley shows that baskets were water-proofed with bitumen before 5,500 BCE in Mehrgarh, an ancient site located in present-day Pakistan between the cities of Quetta, Kalat, and Sibi.

Bitumen is mentioned in some of the earliest records, specifically those written on tablets as early as 3,200 BCE; the tablets were discovered in the ancient city of Sumer. Bitumen use is also mentioned in Egyptian pictographs that were written at roughly the same time. Sumer was the leading city of the Sumerian civilization, which arose in about 3,500 BCE in Mesopotamia—"the land between two rivers"—and lasted until about 1,900 BCE. The two rivers are the Tigris and Euphrates, located in present-day Iraq.

Sumerian writings describe the use of bitumen for mortar, to cement eyes into carvings, for building roads, for caulking ships, and in other waterproofing applications [24]. The asphalt came from nearby oil pits, and great quantities of it were found on the banks of the river Issus, one of the tributaries of the Euphrates.

The Greek historian Herodotus mentioned the use of bitumen in Babylon (1,900–1,600 BCE), including for construction of the famous Tower [25]. From about the same time (3,200 BC), Egyptian writings described the use of pitch to grease chariot wheels and asphalt in mummification, primarily to water-proof the strips of cloth in which the mummies were wrapped. For Egyptians, a primary source of bitumen was the Dead Sea, which the Romans called Palus Asphaltites (Asphalt Lake).

The Chinese may have been the first to use petroleum as a source of light and heating, as far back as 1,500 BCE. Petroleum and natural gas were discovered by accident when Chinese miners were drilling for salt. Confucius wrote in 600 BCE about using bamboo poles to build pipelines and drill 100-foot natural gas wells. In 347 CE, Chinese workmen were producing oil and gas from bamboo-drilled wells with leather valves. Many of the same concepts are being used today (with modern materials). Bitumen was slowly boiled to get rid of lighter fractions, leaving behind a thermoplastic material with which scabbards and other items were covered. Statuettes of household deities were cast with this type of material in Japan, and probably also in China.

Ancient Persian tablets tell about using bitumen and its fractions for lighting, topical ointments, and flaming projectiles. It is likely that the light fractions were recovered with simple batch distillation apparatus similar to those described by Zosimus, an alchemist who lived at the end of the 3rd and beginning of the fourth century AD [26]. By 500 BC, it was known that light fractions, such as naphtha could be used not just for illumination, but also as a supplement to asphalt, making the latter easier to handle.

Greek fire was invented during the reign of Constantine IV Pogonatus (668–685) by Callinicus of Heliopolis, a Jewish refugee from Syria. This formidable incendiary weapon was hurled from siphons onto enemy ships, where it burst into flame on contact with air. It could not be extinguished with water. In 674–678 AD, Greek ships used the weapon to defend Constantinople (today's Istanbul, Turkey), crippling the Arab fleet that was attacking the city [27]. The composition of Greek fire was kept as a top secret and remains a matter of speculation and debate. Many scholars believe Greek fire was a viscous liquid composed of naphtha, liquid petroleum, bitumen, and quicklime.

In more recent times, the French extracted oil from oil sands in the 1700s. In the United States and Canada, oil appeared in brine wells and was recovered by skimming.

In the 1840–1850s, most home-based lamps burned whale oil or other animal fats. Historically, whale-oil prices had fluctuated wildly, but they peaked in the mid-1850s. By some estimates, due to the over-hunting of whales, in 1860, several species were almost extinct. Whale oil sold for as much as US$1.77 per gallon, equivalent to about US$66 per gallon ($2,900 per barrel) in 2021 [28]. In contrast, lard oil sold for about US$0.90 per gallon. Lard oil was more abundant, but it burned with a smoky, smelly flame.

The modern petroleum era began in the 1840s, when various people obtained oil by heating coal in the absence of oxygen. In 1847, James Oakes built a "rock oil" refinery in Jacksdale, England, to recover "paraffin oil" from coal for use in lamps. Also in 1847, James Young, a Scottish chemist, distilled lamp oil from natural seep oil; his technique also produced lubricating oil and paraffin wax. Young obtained a patent on his process in 1850. That same year, Young and Edward Binney formed a partnership named E. W. Binney & Co. at Bathgate in West Lothian and E. Meldrum & Co. at Glasgow. Their Bathgate facility was finished in 1851. Meanwhile, Canadian geologist Abraham Gesner distilled kerosene from crude oil in 1848. In 1850, Gesner created the Kerosene Gaslight Company and began installing lighting in the streets in Halifax and other cities. Later in the United States, he founded the North American Kerosene Gas Light Company on Long Island, New York.

Oakes's paraffin oil, Young's lamp oil, and Gessner's kerosene burned more cleanly than lard oil, and they were far less expensive than whale oil.

In the 1850s, Ignacy Łukasiewicz and Robert E. Dietz independently developed practical kerosene lamps. Dietz invented a flat-wick lamp in 1857. The Dietz lamp was arguably the most successful of several devices designed to burn oils other than animal fats. Łukasiewicz was a pharmacist in Lvov, Poland. In 1852, he and his assistant, Jan Zeh, experimented with ways to improve the safety of burning seep oil obtained from the Carpathian Mountains. From a local peasant, they learned how to boil away the most volatile components. With their own experiments, they devised ways to remove heavy impurities. Working with a local tin smith, they developed a lamp that burned the purified fuel with a clean, steady flame. Łukasiewicz illuminated the window of the pharmacy with one of the lamps. This became significant when the local hospital needed light for a nighttime surgery. A hospital employee had seen the Łukasiewicz lamp and suggested using it. It was so successful that the hospital purchased others, which were installed on July 31, 1853 a date that is now celebrated as the birth of the Polish petroleum industry. Word spread. By 1858–1859, Łukasiewicz/Zeh lamps were replacing other forms of illumination in Austrian railway stations. In 1854, Łukasiewicz moved to Southern Poland, where he collaborated with a partner to develop an oil field near Bobrka. His first wells were dug with picks and shovels and reinforced by wood beams. The deepest was 150 m (480 ft). During subsequent years, he opened several more oil wells, and in 1859, he commissioned a refinery near Jasło [29].

Several people are given credit for the first modern oil well. An early well was drilled in 1848 by F. N. Semyenov in Azerbaijan. Eleven years later, an actual oil refinery was constructed near the well to convert the raw materials into desired products. The first Łukasiewicz well was dug in 1854. Some claim that the first well was drilled in 1857 by the American Merrimac Company in Trinidad to a depth of 280 feet. Canadians claim that the first true oil well in North America was drilled in Petrolia, Ontario in 1858. Meanwhile, in 1855, Benjamin Silliman Jr., a professor of chemistry at Yale University, issued an exhaustive report that may have been the first formal petroleum assay. Hired by the Pennsylvania Oil Rock Company to analyze samples of petroleum, he determined (among other things) that 50% of a petroleum sample could be distilled into flammable oils and 40% could be employed for lubrication and gas lighting. He also noticed the peculiar breaking up of the heavier oils into lighter products, under the continued action of heats far below their boiling points; that phenomenon is now called "cracking." He remarked that when "exposed for many days in an open vessel at a regulated heat below 112°F, the oil … gradually and slowly disappeared, and finally leaving a small dark and pitchy residue." He was the first to demonstrate the high value of the rectified oil as an illuminant, employing a lamp which is the prototype of the kerosene lamps which have been devised since that time [30].

The availability of kerosene got a sudden boost on August 27, 1859, when Edwin L. Drake struck oil with the well he was drilling near Titusville, Pennsylvania. By today's standards, the well was shallow—about 69 feet (21 m) deep and it produced only 35 barrels per day. Drake was able to sell the oil for US$20 per barrel, a little less than the price of lard oil and 70% less than the price of whale oil.