

HAROLD H. SCHOBERT

# Chemistry of Fossil Fuels and Biofuels

CAMBRIDGE

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## **Chemistry of Fossil Fuels and Biofuels**

Focusing on today's major fuel resources – ethanol, biodiesel, wood, natural gas, petroleum products, and coal – this book discusses the formation, composition and properties of the fuels, and the ways in which they are processed for commercial use. The book examines the origin of fuels through natural processes such as photosynthesis and the geological transformation of ancient plant material; the relationships between their composition, molecular structures, and physical properties; and the various processes by which they are converted or refined into the fuel products appearing on today's market. Fundamental chemical aspects such as catalysis and the behaviour of reactive intermediates are presented, and global warming and anthropogenic carbon dioxide emissions are also discussed. The book is suitable for graduate students in energy engineering, chemical engineering, mechanical engineering, and chemistry, as well as for professional scientists and engineers.

**Harold H. Schobert** is Professor Emeritus of Fuel Science, The Pennsylvania State University, and Extra-ordinary Professor, Coal Research Group, North-West University. A recognized leading authority on energy technology, he has over 30 years' experience in teaching and research on fuel chemistry.

“The book is a welcome modern update to the available literature regarding the genesis, characteristics, processing and conversion of fossil and bio-derived fuels. Its comprehensive coverage of the chemistry involved with each of these aspects makes it an important source for upper-level undergraduates, graduate students, and professionals who need a strong understanding of the field. It is an interesting read for anyone who really wants to understand the nature of fuels.”

*Robert G. Jenkins, University of Vermont*

“There is no other book like this in field of energy science. It is the perfect introduction to the topic; but Professor Schobert has packed so much in, that it is just as much a valuable reference for more experienced professionals. It touches on all aspects of fuel formation, transformation and use as well as strategies for managing the end product, carbon dioxide. I will be using it as a text in my own teaching to both senior undergraduate and graduate students.”

*Alan L. Chaffee, Monash University, Australia*

“This is an excellent reference for the student of modern fuel science or the practitioner wishing to sharpen their ‘big-picture’ understanding of the field. The book offers a seasoned balance between technical rigor and readability, providing many helpful references for the reader interested in further study. I found the text engaging and enlightening, with the end-of-chapter notes a particularly thought-provoking and entertaining bonus.”

*Charles J. Mueller, Sandia National Laboratories*

# 10 Composition, properties, and processing of natural gas

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Natural gas is a mixture of hydrocarbons with various quantities of non-hydrocarbons, which exists either in the gas phase or in solution with petroleum in natural underground reservoirs. The principal hydrocarbon component is methane. In most parts of the world, by the time the gas has been treated and distributed to consumers, it consists almost entirely of methane.

Gas produced during catagenesis usually migrates through porous rocks in the Earth's crust until it encounters a formation of non-porous rock. This non-porous rock prevents further migration of the gas, effectively trapping it in the porous rock below. The porous rock becomes a reservoir for the gas. The gas can be classified according to how it is found. *Associated gas* is found in conjunction with accumulated oil, either dissolved in the oil, called *dissolved gas*, or as a separate gaseous phase above the oil, *gas-cap gas*. *Non-associated gas* is found without accompanying oil. A reservoir of non-associated gas could arise from gas migrating to a different location than that to which oil migrated, or from formation of gas in the gas window, i.e. without oil. About 60% of the world's natural gas is non-associated.

Other sources of methane-rich gases occur in nature. Biogenic gas, produced during diagenesis, comes from the action of anaerobic bacteria on accumulated organic matter. Landfill gas is produced in the same way, but differs in that the feedstock is the organic residues of civilization, accumulated as solid waste in landfills. Excrement from humans or other animals also reacts in the same way, providing a useful source of fuel for farms or even domestic use [A]. Methane forms and accumulates in coal seams; its deliberate removal prior to mining provides another source, coalbed methane.

Two other methane sources may offer enormous reserves of fuel. Shale gas is produced in shales (laminated, compacted sediments of clay or silt) that were rich in kerogen and that have experienced catagenesis conditions typical of the oil window. Unlike conventional oil source rocks, the shales have so little permeability that gas does not migrate, but remains adsorbed in the pores and natural fractures of the shale. Many countries around the world have shales that are either already sources of gas, or potential sources in the future. A very different, but also unconventional, source lies on the sea floor or in the tundras of the far North. At low temperatures, water molecules associate in cage-like structures large enough to accommodate small molecules in their interior. Methane can be trapped in this way. The generic structures are known as clathrate hydrates; when methane is the entrapped molecule, they are called natural gas hydrates or methane hydrates [B]. Optimistic estimates suggest that possibly 2500 Gt of methane is trapped in hydrates on the sea floor, and another 500 Gt in hydrates in the permafrost in northern tundras. This amount exceeds by an order of magnitude all the other known natural gas reserves [C]. World consumption of natural gas in 2007 was about 2.7 Gt.

**Table 10.1** Normal boiling points of the *n*-alkanes and 1-alkenes up to C<sub>6</sub>.

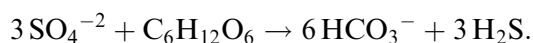
<i>Compound</i>	<i>Normal boiling point, °C</i>
Methane	-162
Ethane	-88
Ethylene	-104
Propane	-42
Propene	-48
Butane	-0.5
1-Butene	-6
Pentane	36
1-Pentene	30
Hexane	69
1-Hexene	63

Depending on where in the oil or gas window a particular natural gas formed, it might contain other light alkanes and alkenes. Thermal cracking during catagenesis gives rise to a variety of other gaseous products in addition to methane. Two types of natural gas can be found: one in which methane is essentially the only hydrocarbon component, and one that contains not only methane but other small alkanes and alkenes. As discussed in the next section, there are significant differences in boiling point among these small hydrocarbons (Table 10.1).

These volatility differences make it relatively easy to condense components heavier than methane. Gases can be classified as dry gas, essentially pure methane, and wet gas, for which the condensable hydrocarbons amount to greater than 0.040 l/m<sup>3</sup>. In this context, the terms *wet* and *dry* have nothing to do with water – they refer only to the presence or absence of condensable hydrocarbons. Hydrocarbons recovered from wet gas can be separated by processes that are discussed later in this chapter, and themselves represent useful materials. Ethane is converted to ethylene, the most important feedstock for the petrochemical industry. Propane and butane are useful fuel gases in their own right, propane being the principal component of LPG, liquefied petroleum gas.

Condensable hydrocarbons that are liquid at ambient temperature make up natural gasoline (sometimes also known as casinghead gasoline, or as pentanes-plus), which can be used as a petrochemical feedstock or blended with other gasoline sources in a refinery. The composition of natural gasoline varies from one source to another. Generally it consists of pentane and larger hydrocarbons, though some samples can contain appreciable amounts (i.e. a few tens of percent) of butane.

Some natural gas deposits contain hydrogen sulfide, usually in small amounts [D]. Such gas is known as sour gas. Hydrogen sulfide can arise in several ways. Some amino acids contain the thiol group, e.g. cysteine, HSCH<sub>2</sub>CH(NH<sub>2</sub>)COOH. Anaerobic decay of proteins containing such amino acids liberates H<sub>2</sub>S. The sulfate ion, second only to chloride in concentration of anions in saline waters, undergoes anaerobic microbial reduction, e.g.

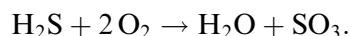
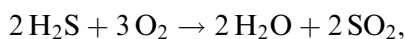


If sulfur, regardless of source, survives diagenesis it can be incorporated into various organic compounds in kerogen. Then, thermal decomposition of sulfur-containing

compounds could occur during catagenesis. Sulfur occurs in organic compounds in many kinds of functional group; however, the C–S bond has a lower dissociation energy than the C–O bond, so these groups are likely to be lost, possibly via reactions analogous to those discussed in Chapter 8 for oxygen functional groups. As an example, thermally induced desulfurization of a thiol can be represented as

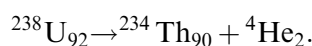


Sour gas presents several problems. Hydrogen sulfide itself has a dreadful smell (it is the gas responsible for the characteristic odor of rotten eggs), and, worse, is poisonous. A concentration in air of only 15 parts per million represents the short-term exposure limit, i.e. to which exposure for fifteen minutes could lead to serious health effects. Hydrogen sulfide dissolves in water to form a mildly acidic solution that can corrode metallic components of gas handling and storage systems. Hydrogen sulfide present in the gas when it is burned is converted to the sulfur oxides:

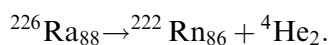


Release of these oxides to the atmosphere is followed by their eventually being washed out of the atmosphere, reducing the pH of the precipitation. This results in the serious environmental problem commonly known as acid rain [E]. Processes that remove hydrogen sulfide from natural gas are collectively known as sweetening, and are discussed later in this chapter.

Some natural gas deposits also contain the noble gases, helium being the most important. Natural gas deposits with up to  $\approx 8\%$  helium are known. In the United States, the principal commercial source of helium is the natural gas found in the Texas panhandle, which has  $\approx 2\%$  helium. Other significant sources occur in Algeria and possibly Qatar. Helium derives from radioactive decay of isotopes of uranium, thorium, and radium in the Earth's crust, for example



Smaller amounts of the other noble gases can also occur in natural gas, argon and radon [F] being examples. Radon also originates from radioactive decay of uranium, thorium, or radium, e.g.



Helium is recovered by a sequence of cryogenic processes. The natural gas is first cooled sufficiently to condense the hydrocarbons, leaving a mixture of nitrogen and helium in the gaseous state. Further cooling causes the nitrogen to condense. The remaining gas is passed through activated carbon adsorbents at liquid nitrogen temperature, i.e.  $-196^\circ\text{C}$ .

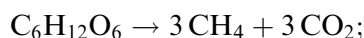
Hydrogen occurs, albeit rarely, in some natural gas deposits. Its formation with natural gas may be due to dehydrogenation reactions late in catagenesis. Hydrogen is a remarkably mobile material that readily finds its way through any pores, cracks, or other leaks in rock formations (or in process equipment, for that matter). Small amounts of hydrogen that might form can often escape into the atmosphere, where Earth's gravitational field is not adequate to retain it.

Carbon dioxide usually – but not always – is a minor component of natural gas. Carbon dioxide can account for 50% or more of the natural gas in, e.g. Mexico,

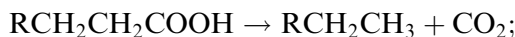
**Table 10.2** Examples of natural gas composition (volume percent) from various sources. Data for butanes and pentanes include both *n*- and iso- compounds; “hexanes+” includes hydrocarbons of C<sub>6</sub> and larger. NR – not reported.

<i>Constituent gas</i>	<i>Algeria</i>	<i>Canada (western)</i>	<i>Denmark</i>	<i>Thailand</i>	<i>USA (Penna.)</i>
Methane	83.0	95.2	87.2	72.4	88.2
Ethane	7.2	2.5	6.8	3.5	11.0
Propane	2.3	0.2	3.1	1.1	1.9
Butanes	1.0	0.06	1.0	0.5	0.79
Pentanes	0.3	0.02	0.17	0.1	0.26
Hexanes+	NR	0.01	0.05	0.07	0.11
Helium	0.2	NR	NR	NR	0.10
Hydrogen	NR	Trace	–	NR	0.003
Nitrogen	5.8	1.3	0.3	16.0	3.04
Carbon dioxide	0.2	0.7	1.4	6.3	0.02

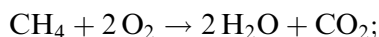
Pakistan, and the North Sea. Several processes account for the production of carbon dioxide, including anaerobic decay reactions:



decarboxylation reactions:



oxidation of hydrocarbons by oxygen dissolved in surface waters that percolate through the reservoir:



and possibly the thermal decomposition of carbonate rocks strongly heated by contact with magma:



The composition of natural gas as it comes from the well varies quite a bit around the world. Table 10.2 shows the composition of samples of natural gas from different parts of the world.

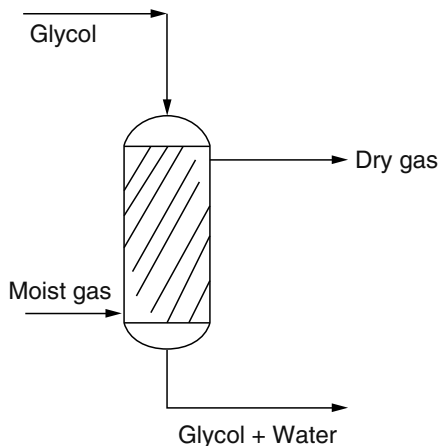
## 10.1 Gas processing

Several processing or purification steps are usually applied to natural gas before it is put into a pipeline system for sale to consumers. These operations focus on removing those components other than methane: water, hydrogen sulfide, and other hydrocarbon gases. The amount of processing, and the specific processing steps used, depend on the composition of the gas as it comes from the well.

### 10.1.1 Dehydration

Dehydration is usually the first step in gas processing. It is done for several reasons: some of the subsequent processing steps operate below 0°C; any water present would freeze to ice while the gas was being treated. Moisture in the gas in the distribution





**Figure 10.1** A simple process for gas dehydration using one of the glycols as the dehydrating agent.

and storage systems could cause “icing” of valves, gauges, and fuel lines during cold weather. Condensation of vapor to liquid water can accelerate corrosion, because hydrogen sulfide and carbon dioxide dissolve into the liquid to produce mildly acidic solutions.

Water vapor can be removed by absorbing it into liquids, or adsorbing it onto the surfaces of solids. Both approaches have merit, and both are used commercially. Gas dehydrators are tanks or towers in which the gas is brought into contact, usually in countercurrent flow, with compounds that absorb moisture. Such compounds include diethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ; triethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ; or tetraethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ . Of these, triethylene glycol is the dominant choice, though the others certainly work well. Use of the glycols relies on two properties: first, the abundance of oxygen atoms in these molecules provides numerous sites for absorbing and retaining water molecules via hydrogen bonding. Hydrogen atoms in the hydroxyl groups at the ends of the molecules can hydrogen bond to water molecules, while the oxygen atoms in the ether groups in the interior of the molecules can accept hydrogen bonds from water molecules. Second, these glycols have very low vapor pressure. This means that the gas stream, during treatment, is not contaminated with a new impurity (i.e. glycol vapors) while the moisture is being removed.

Figure 10.1 presents a flow diagram of a dehydration process. Gas containing moisture is brought into contact with the dehydrating agent in a countercurrent flow absorber. Water is transferred into the dehydrating agent, producing the desired stream of dried gas, along with a solution of water in, say, triethylene glycol. Economy of operation requires that the glycol be recovered and recycled. Options for regenerating the glycol include treating it in vacuum to draw water off as a vapor for subsequent condensation, or stripping the glycol by passing through it some vapor that will not react with glycol under these conditions.

The alternative approach relies on the adsorption of water vapor onto the surface of solids. In this application, adsorption results from van der Waals interactions of water molecules with the surface of the adsorbent (also called the desiccant). The use of solids is preferred in two specific cases. One is in relatively small-scale applications, where the



simplicity and ease of operation, as described below, are advantageous. The other is when essentially complete dehydration of the gas is required.

Several kinds of solid can be used in this application, including silica gel, activated alumina, activated bauxite, and molecular sieves. Silica gel is a colloidal form of silicon dioxide, which, because of its high surface area per unit mass, finds many applications as a dehydrating agent. Many electronic and optical goods come with a small packet of silica gel in the packaging, to prevent water vapor from condensing on the items during shipping and storage. Activated alumina is a granular form of aluminum oxide having high porosity, so this also has a high surface area available for adsorption. Activated bauxite is similar, but has other constituents in addition to the aluminum oxide, such as iron oxide or clays. (Bauxite is better known as the ore that is the principal source of aluminum.) Molecular sieves are natural or synthetic zeolite minerals [G] having pore sizes small enough to allow certain molecules to enter or pass through the solid, while excluding molecules of larger size; in this regard they operate on a molecular level analogously to an ordinary sieve used to separate particles of different size, such as rocks from sand.

The simplest adsorption system would involve a vessel containing a bed of adsorbent, with provision for the gas to pass through the bed. A point is reached at which the adsorbent has taken up so much water that it has reached the limit of its capacity, and must be regenerated before it can be used further. Regeneration can be accomplished with a flow of hot gas through the bed. A more practical system would use two vessels in parallel, so that one can be in use adsorbing water while the other is being regenerated.

### 10.1.2 Gas sweetening

The several negative characteristics of hydrogen sulfide make sweetening the most important single process in gas treatment. Not surprisingly, numerous approaches have been developed.

Useful absorbents for hydrogen sulfide come from the family of alkanolamines. The simplest is monoethanolamine (MEA),  $\text{HOCH}_2\text{CH}_2\text{NH}_2$ . These compounds contain both alcohol and amine functional groups. Other compounds in this family suitable for sweetening include diethanolamine (DEA),  $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ , and diisopropylamine (DIPA),  $((\text{CH}_3)_2\text{CH})_2\text{NH}$ . Sweetening operations using these reagents rely on the fact that, as a weak acid, hydrogen sulfide can be absorbed and retained by bases. As with dehydration, removal of one impurity, i.e.  $\text{H}_2\text{S}$ , should not add a new one to the gas stream. Thus reagents for sweetening should be mild bases with low vapor pressures, specifications which diethanolamine meets well:

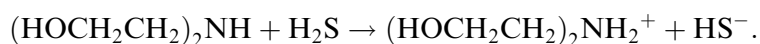
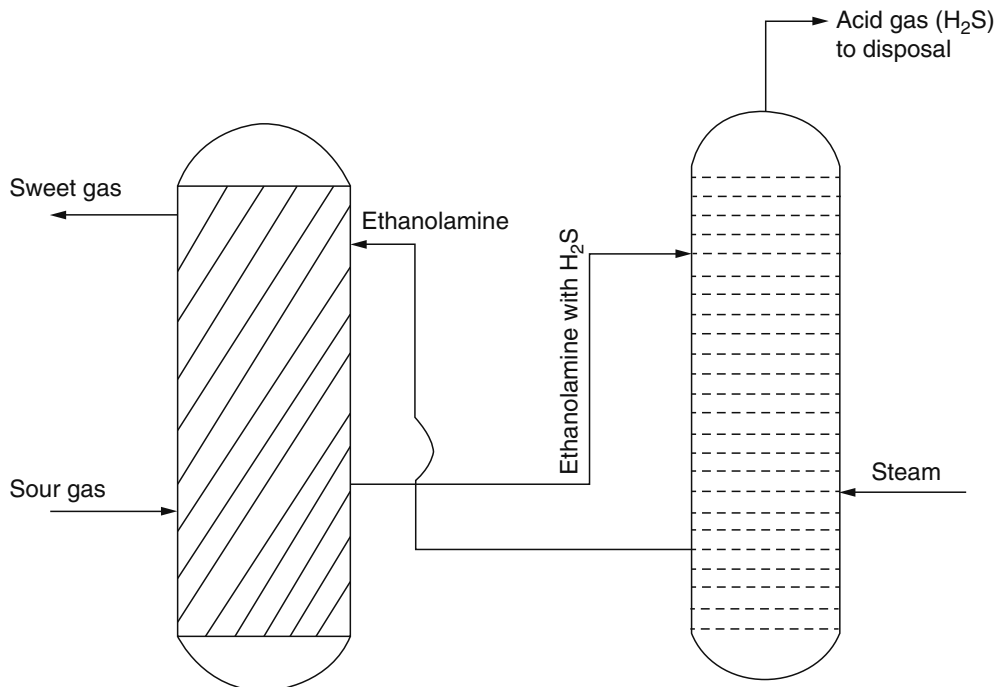
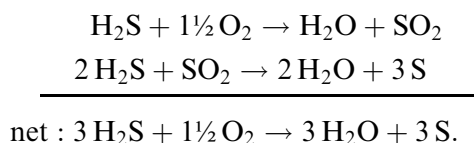


Figure 10.2 illustrates the process flow scheme for sweetening with alkanolamines. Sour gas contacts the alkanolamine in countercurrent flow. The alkanolamine–hydrogen sulfide solution, referred to as the “rich” solution, proceeds to a stripping column, where it is treated with steam to remove hydrogen sulfide, and any carbon dioxide that may also have dissolved in the alkanolamine. The “lean” alkanolamine is then recycled back to the absorber. The mixture of hydrogen sulfide and carbon dioxide, collectively referred to as acid gases (because they both dissolve in water to form mildly acidic solutions), is passed to a disposal process, such as the Claus process, which is discussed below and later in Chapter 20.

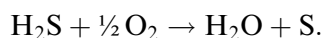


**Figure 10.2** A gas sweetening process using ethanolamine as the sweetening agent, followed by steam stripping to liberate the  $\text{H}_2\text{S}$  and regenerate the ethanolamine.

When the  $\text{H}_2\text{S}$  content of the gas is very high, there can be value in recovering the sulfur and selling it to, e.g. sulfuric acid manufacturers. The Claus process [H] provides a way of doing this. In a sense, the Claus process can be thought of as mainly a sulfur-production process, and not a process used specifically for sweetening. The Claus process is often used downstream of other processes that remove hydrogen sulfide from the gas. Recovery of sulfur depends on oxidation of hydrogen sulfide to sulfur, in two steps:



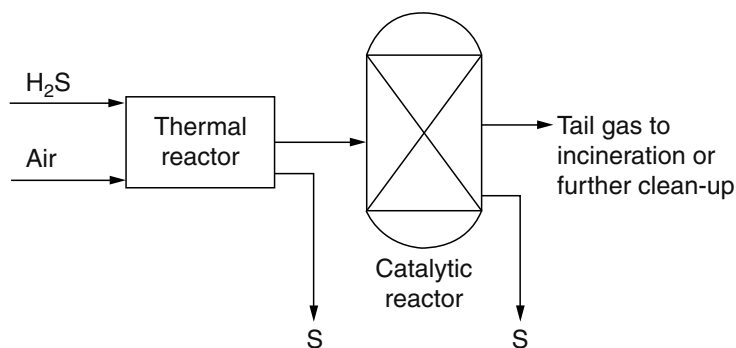
The first reaction can be accompanied by direct reaction of  $\text{H}_2\text{S}$  to sulfur, i.e.



Both reactions of hydrogen sulfide with oxygen are thermal processes, occurring above  $550^\circ\text{C}$ . The reaction of hydrogen sulfide with sulfur dioxide is a catalytic process at  $\approx 370^\circ\text{C}$ . Activated alumina is a useful catalyst.

A process flow diagram is shown in Figure 10.3.

With three catalytic reactors, about 97% of the hydrogen sulfide can be converted to sulfur. Depending on the air quality standards where this plant is operating, the residual sulfur gases (which might include small amounts of carbonyl sulfide and carbon disulfide) and any carbon dioxide present are emitted to the atmosphere. Otherwise, these so-called tail gases from the Claus unit must be treated further to reduce the sulfur emissions even further.



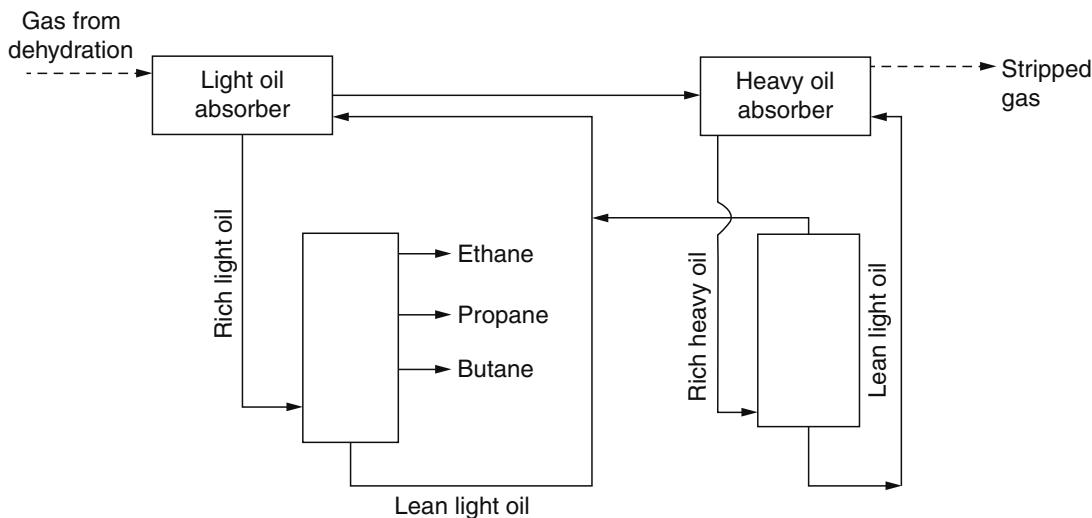
**Figure 10.3** The Claus process consists of partial conversion of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  in a thermal reaction, followed by a catalytic reaction of  $\text{SO}_2$  with  $\text{H}_2\text{S}$ .

### 10.1.3 Separation of $\text{C}_2^+$ hydrocarbons

If the gas is also wet, the sweetened gas is passed through a light oil absorber. In this unit, the gas is brought into contact with hexane at  $-20^\circ\text{C}$  and 3.5 MPa. Since hydrocarbons are neither acidic nor basic, nor capable of hydrogen bonding, strategies used in dehydration and sweetening cannot be used. Instead, the approach is to dissolve the hydrocarbons in a suitable solvent. Based on the rule-of-thumb that “like dissolves like,” hexane makes a good solvent for the lighter alkanes. Temperature and pressure conditions are chosen on the basis of the increasing solubility of gases in liquids with decreasing temperature and increasing pressure. The solution of light hydrocarbon gases in hexane is called rich light oil. Fractional distillation of the rich light oil yields ethane, propane, and butane. Unlike the glycols and the ethanolamines, some hexane vapors inevitably appear in the gas. A heavy oil absorber removes the hexane.

Fractional distillation of the condensate from wet gas makes it possible to recover ethane and propane as pure fractions. The distillation must be performed at elevated pressure, to keep some of the components in the liquid phase. The major use of ethane is in the production of ethylene, which in turn is used in enormous amounts ( $\approx 110$  million tonnes per year) by the petrochemical industry for making such polymers as polyethylene and poly(vinyl chloride) that are nearly ubiquitous in modern life. Ethane heated in the presence of steam to  $>900^\circ\text{C}$  dehydrogenates to ethylene [I]. At atmospheric pressure propane boils at  $-42^\circ\text{C}$ , so that it liquefies reasonably easily to, and constitutes the principal component of, LPG.

Natural gasoline can be recovered either by compressing the gas stream until the pressure becomes high enough to liquefy the relatively non-volatile higher alkanes, or by distillation of the liquid from the heavy oil absorber. Natural gasoline can be used as an additive to the gasoline obtained from petroleum distillation, particularly to enhance the vapor pressure of the blend, improving cold-weather starting. Natural gasoline is of relatively low octane number,  $\approx 65$ , not by itself giving good performance in modern high-compression engines. Nonetheless, natural gasoline is used directly as a liquid vehicle fuel in some parts of the world. Nowadays the natural gasoline not used as a blend stock is sold for petrochemical production, primarily for conversion to ethylene. Like natural gas itself, the composition of natural gasoline varies widely from one source to another. In general, the principal components include 30–80% of  $\text{C}_5$



**Figure 10.4** A flow diagram for a process that removes the larger gaseous hydrocarbons from methane.

hydrocarbons, i.e. pentane, isopentane, and 2,3-dimethylbutane; 15–40%  $C_6$  hydrocarbons, hexane, 2- and 3-methylpentane, methylcyclopentane, and cyclohexane; a small amount,  $\approx 1\%$ , of benzene; 5–30%  $C_7$  hydrocarbons such as heptane, the methylhexanes, dimethylcyclopentanes, and methylcyclohexane; a few percent of toluene; and about 5% of the various  $C_8$  hydrocarbons.

Butane and 2-methylpropane (isobutane), referred to as the  $C_4$  cut, are easily liquefied. Butane boils at  $-1^\circ\text{C}$ . Only a slightly elevated pressure,  $\approx 230$  kPa, is needed to keep it in the liquid phase at ambient temperature. The liquid fuel visible in transparent cigarette lighters is butane. Pentane, 2-methylbutane (isopentane) and 2,2-dimethylpropane (neopentane) comprise the  $C_5$  cut. Depending on the composition and quality of these products, they are used for gasoline blending or for ethylene production.

Figure 10.4 illustrates a sequence of gas processing steps.

After this sequence of operations, the product is sometimes called stripped gas. With addition of small quantities of an odorant, it is finally ready to go into the pipeline for sale to consumers.

Natural gas as eventually supplied to consumers is typically  $>90\%$  methane, and often close to 100% methane. Methane is both invisible, mixing freely with air, and has no odor. It is also highly flammable, and in  $\approx 5\text{--}15\%$  mixtures with air, explosive. Some simple way is needed to determine whether natural gas is leaking, to avoid potentially tragic situations [J]. This is done by adding an odorant, so that a natural gas leak can be detected by smell. The odorant is usually a small organic sulfur compound, or mixture of such compounds. A popular component of odorant blends is 2-methyl-2-propanethiol (*tert*-butyl mercaptan), a compound with the rather noticeable aroma of rotten cabbage. While it may seem counterproductive to put sulfur compounds back into a sweetened gas, the small mercaptans and the related sulfides have such horrendous odors that they can be detected easily at the parts-per-million level. The tiny amount of  $\text{SO}_x$  produced when the odorant burns is negligible.

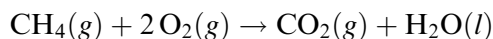
**Table 10.3** Comparison of the contributions of the heats of formation of carbon dioxide and water to the observed calorific values of selected fuels, in kJ per mole of carbon.

<i>Fuel</i>	<i>CO<sub>2</sub> contribution</i>	<i>H<sub>2</sub>O contribution</i>	<i>Total</i>
CH <sub>4</sub>	-393	-570	-963
C <sub>10</sub> H <sub>22</sub>	-393	-314	-707
C <sub>100</sub> H <sub>80</sub>	-393	-114	-507

## 10.2 Natural gas as a premium fuel

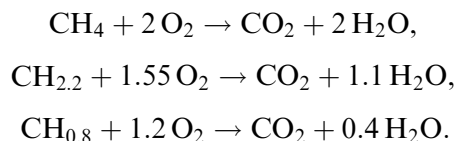
By several criteria, natural gas is *the* premium fuel. On an equal mass basis, combustion of natural gas liberates more energy than any other hydrocarbon fuel [K]. It also produces less carbon dioxide per unit of energy, 0.05 kg CO<sub>2</sub>/MJ. It contains no inorganic, ash-forming components, so leaves no residue on combustion. Sour gas can be sweetened easily, eliminating the problem of sulfur emissions during combustion. Fluids are much easier to handle, meter, and regulate in process or combustion systems than are solids. The low density of gases at ordinary conditions does make it difficult to store a useful weight of gaseous fuel, unless it is compressed to high pressure or stored cryogenically as a liquid. Nevertheless, most natural gas consumers, especially domestic users, can connect directly to the distribution system, eliminating the requirement for on-site storage commonly needed with other fuels.

For pure methane, the enthalpy change for the reaction



is -892 kJ/mol. In the initial combustion process reaction temperatures are high enough such that the water produced in the reaction is in the gaseous state (i.e. steam). Several factors contribute to natural gas having the highest calorific value among the common fuels. One, the hydrogen content, is discussed here; others recur later in this book. Taking natural gas, as delivered to the consumer, essentially to be pure methane, its H/C ratio is 4. Many petroleum products have H/C of  $\approx 2$ . Decane, C<sub>10</sub>H<sub>22</sub>, can be taken as a representative component of light petroleum products. For humic coals, H/C < 1. We see in Chapter 17 that coals have complex, macromolecular structures, but for now it can be assumed that coal can be represented by the formula C<sub>100</sub>H<sub>80</sub>. If these fuels are burned in oxygen to produce carbon dioxide and liquid water, the enthalpy liberated is that contributed by the formation of these two products, minus the enthalpy of formation of the fuel. The heats of formation of the products are -393 and -285 kJ/mol, respectively. Real petroleum products contain dozens, possibly hundreds, of components, so that the heat of formation can only be represented as a weighted average of the heats of formation of the components, if we know what they are. The heat of formation of coal is a term rarely considered in coal science or technology. To simplify, heats of formation are neglected, and only the contributions of the CO<sub>2</sub> and H<sub>2</sub>O(*l*) to the overall heating value are considered. And, to make a fair comparison among these fuels, it is helpful to compare on the basis of an equal number of moles of carbon,

i.e.  $\text{CH}_4$ ,  $\text{CH}_{2.2}$ ,  $\text{CH}_{0.8}$ . For these hypothetical molecules the combustion reactions can be written as



From this, the contributions of carbon dioxide and liquid water to the enthalpy release can be determined, as summarized in Table 10.3.

Table 10.3 shows that, on the basis of an equal number of moles of carbon, the contribution of the enthalpy of formation of carbon dioxide is the same for each. But the contribution of the enthalpy of formation of water decreases, because the amount of hydrogen in the original fuel has decreased from  $\text{CH}_4$  to  $\text{CH}_{2.2}$  and again to  $\text{CH}_{0.8}$ . This analysis leads to a useful rule of thumb for comparing hydrocarbon fuels: among a group of fuels compared on an equal amount of carbon, the heating value decreases as the H/C ratio decreases. Like most such rules, this one is useful only for a quick, qualitative comparison. The analysis shown in Table 10.3 does not consider heats of formation of the reactants. As discussed in Chapter 17, other factors in addition to H/C ratio influence heating value, particularly oxygen content and aromaticity. But, so long as care is taken to apply the rule only to materials that are reasonably similar, it provides a useful, quick assessment. Within a family of compounds that are closely related chemically, and for which the heats of formation of the reacting molecules are known, the relationship of heat of combustion and H/C ratio becomes quite good. Such a relationship for the *n*-alkanes was shown in Figure 9.13.

## Notes

- [A] People in many countries rely on anaerobic digestion of manure and even of human feces as a source of gaseous fuel. They include probably tens of millions of people in China. The digestors are of simple, “low-tech” design, relatively easy to make. And, the residual solids make good fertilizer.
- [B] As an example, twenty water molecules can associate, via intermolecular hydrogen bonding, to form a pentagonal dodecahedron. The interior of this structure has enough volume to accommodate molecules of methane, as well as other gases such as chlorine molecules or atoms of the noble gases. Frozen methane hydrates can be ignited with a match and will burn, giving rise to informal names such as “the ice that burns.” This kind of clathrate formation is not limited to water. For example, aqueous solutions of nickel cyanide can form  $\text{Ni}(\text{CN})_2$  clathrates big enough to trap benzene molecules. In similar fashion, the benzene can be ignited and burned.
- [C] Optimists see this as an immense deposit of fuel for future use. Pessimists note that methane is a potent greenhouse gas, a much better infrared absorber than carbon dioxide, and are concerned that if Earth were to warm enough to cause a sudden and massive release of methane from the permafrost, the rapid addition of large quantities of methane to the atmosphere would cause a step change in global warming.

# 12 Petroleum distillation

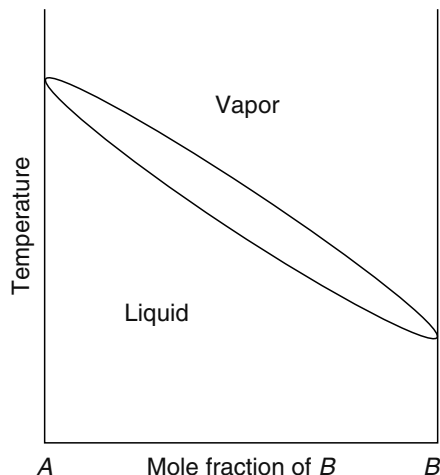
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Petroleum goes through multiple operations intended to separate it into fractions, to improve product quality (e.g. by removing sulfur), and to enhance yields of the more valuable fractions relative to those for which there is less demand. Collectively these operations comprise the technology of oil refining. The objective of refining is to convert petroleum into useful, marketable products through processes that are both economically feasible and environmentally acceptable. Considering on the one hand the complexity and variability of petroleum, and on the other hand the demands imposed for meeting economic and environmental criteria, it is remarkable that petroleum products cost us, the consumers, as little as they do. The primary products of refining are liquid fuels mainly used in the transportation sector, and to a lesser extent for space heat, process heat, or raising steam for electricity generation. Secondary products include feedstocks for the chemical and polymer industries, and carbon materials. The refining situation faces a third constraint, in that the quality of the crude oil available to refineries is slowly but steadily decreasing. Over a century, the API gravity of crudes processed in refineries has dropped from 30–40°, typical of oils processed in the late nineteenth century, to 15–30° by the end of the twentieth century.

Generally, the desirable and valuable products that can be made from petroleum have H/C ratios higher than those of the petroleum itself. Two strategies provide routes to these products. One is to increase the hydrogen content by adding hydrogen from an external source. Examples include hydrogenation (e.g. conversion of aromatics to cycloalkanes) and hydrocracking, discussed in Chapter 15. The alternative involves removing carbon, known as carbon rejection. The folk saying “If you can’t raise the bridge, lower the river” relates directly; the numerical value of any ratio can be increased by increasing the numerator or reducing the denominator. Many thermal processes discussed in Chapter 16 yield, in addition to the desired light products, highly aromatic tars or solid carbonaceous residues as the rejected carbon.

Petroleum has virtually no applications in which it is used directly as it comes from the ground [A]. Near the well site, it can be used “as-is” in furnaces or diesel engines adapted to the characteristics of that particular oil. But the most efficient use of fuel throughout the energy sector requires both a narrow range of properties and consistent properties, so that engines or stationary equipment can be designed for optimum utilization of a specific fuel. Petroleum consists of tens of thousands of compounds. The narrowest range of properties, and the utmost in consistency, can be achieved by using pure compounds as fuels. In principle, though probably with great difficulty in practice, each of the components of petroleum could be separated and recovered, one by one. Since most are present in very low concentration, <1%, and since many have similar chemical and physical properties, the separation processes are likely to be





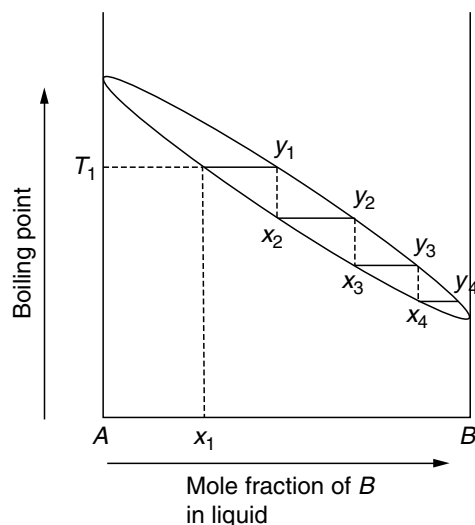
**Figure 12.1** A vapor–liquid equilibrium diagram for a hypothetical binary system of components *A* and *B*, where *B* is the more volatile (lower-boiling).

inefficient, tedious, and costly. Hypothetical pure-compound fuels would be both in very short supply and very expensive. Therefore, refining of petroleum represents a compromise between, on the one hand, the highly variable composition and properties of the world's oil supplies, and, on the other hand, the considerable expense and difficulty of separating a specific oil into its individual molecular components. Compromise is achieved by separating oil into fractions; each fraction still contains dozens or hundreds of individual components, but because the properties of the components vary only over a limited range, each fraction is of reasonably consistent nature.

## 12.1 Desalting

Sodium chloride represents the most common inorganic contaminant of petroleum, and potentially a very troublesome one. Some geological structures that collect petroleum as it migrates through the Earth include layers of salt, or are capped by salt. Saline water can infiltrate into reservoirs. During the drilling and pumping operations that are part of oil extraction, salt can get mixed with the oil. In subsequent processing, the chloride ion can form hydrochloric acid, which is corrosive to processing equipment. Therefore, the first operation in many refineries is desalting the oil.

Salt concentrations of 0.06 g/l or greater would require the oil to be desalted. In some refineries, all oils are desalted as a matter of routine. The salt is in solution in water that is emulsified with the oil. In some cases, the water may also contain suspended crystals of salt, as well as other inorganic debris, such as flakes of iron oxide rust from pipes or storage tanks. The general approach is to mix the oil with water, and heat it to a temperature that will produce a water-and-oil emulsion, using enough applied pressure to keep the water in the liquid state. The volume of water used is about 3–15% of the volume of the oil. The exact amount of water depends on the gravity of the oil. As examples, for crudes greater than 40° API, about 3–4% of water would be used. Heavier oils, say <30° API, would use 7–10% water. The temperature employed also depends on the oil; a 40° gravity oil and water mixture would be heated to 115–125 °C, whereas the mixture of heavier oil with water would go to about 140–150 °C.



**Figure 12.2** Successive changes in the composition of liquid and vapor of the hypothetical  $A$ – $B$  system effected by fractional distillation; with enough steps it would be possible to produce pure  $A$  and pure  $B$ .

The intent is to dissolve salt in the added water in the course of forming a water-oil emulsion. Then, when the emulsion is “broken,” the water layer, which now contains the salt, can be separated from the oil. The simple approach to separating the emulsion is just to give it time to settle. Allowing the emulsion to flow through a bed of small gravel or sand facilitates coalescence of water droplets. If physical settling is not quick enough, or not complete, various compounds can be added to facilitate separation, examples being long-chain alcohols or fatty acids. Strong electric fields have also been used for breaking the oil-water emulsions.

## 12.2 Principles of distillation

The essence of distillation is vapor–liquid equilibrium. When a liquid containing two (or more) components is heated, the composition of the vapor is different from that of the liquid. The vapor is enriched in the more volatile component(s). Withdrawing the vapor from the system and condensing it produces a new liquid phase with a higher proportion of the more volatile component(s) than was in the original liquid. This provides a means of separating a mixture of liquids based on the relative volatilities of its components.

A two-component liquid mixture suffices to illustrate the principles. Liquids having a greater number of components behave in the same way, though analysis of the problem becomes more complex. Referring to the components arbitrarily as the ever-useful  $A$  and  $B$ , the relationships between vapor composition, liquid composition, and temperature can be illustrated by Figure 12.1.

At any given temperature, the equilibrium compositions of vapor and liquid are different. This can be illustrated by Figure 12.2.

When an  $A$ – $B$  mixture with composition  $x_1$  is heated to its boiling point,  $T_1$ , the vapor at equilibrium is richer in  $B$ , the more volatile of the two components. The liquid is

ideally, a design that has enough flexibility to operate with occasional fluctuations in the amount of oil needing to be distilled.

Criteria or indicators are needed to specify whether a particular separation is, or is not, a good one. One such approach compares the temperatures at which 95% of the lighter product, and at which 5% of the heavier product have distilled. A temperature difference can be calculated as

$$\Delta T = 5\%_{\text{vol}}T_H - 95\%_{\text{vol}}T_L,$$

where  $5\%_{\text{vol}}T_H$  is the distillation temperature at which 5 vol% of the heavier product has distilled, and  $95\%_{\text{vol}}T_L$  at which 95 vol% of the lighter product has distilled. If  $\Delta T > 0$ , it is referred to as a gap, and indicates that the separation between the light and heavy products is good. Alternatively, a  $\Delta T < 0$  is an overlap, indicating poor separation between the fractions.

## 12.3 Refinery distillation operations

### 12.3.1 Atmospheric-pressure distillation

Fractional distillation of oil at atmospheric pressure is *the* primary operation in a refinery. Nothing else happens without this step occurring first. The feed, which normally will have been desalted upstream of distillation, is heated by allowing it to flow through piping enclosed within a furnace. The furnace plus the distillation tower itself make up a distillation unit, sometimes called a pipe still. The oil is heated to a temperature that has a value specifically selected to cause a desired fraction of the oil to vaporize. Specific details vary from refinery to refinery, and probably from one oil to another, but furnace outlet temperatures would be in the range 340–400 °C. What is now a vapor–liquid mixture is then allowed to flow into the distillation tower itself. There, the liquid descends while the vapor rises through the tower.

Partially vaporized feed enters the tower in the so-called flash zone, where no trays are located. The portion of the tower above the flash zone is called the rectifying section, and usually contains most of the trays. Here, the proportion of the less volatile components of the oil is progressively reduced as the vapors ascend the tower. The region below the flash zone is called the stripping section, because there the more volatile components are stripped out of the liquid. The temperature at the exit of the pipe still furnace is chosen so that all of the products to be taken off in the flash zone, and about 20% of the material in the rectifying section, are in the vapor phase. The highest boiling temperature for the heaviest cut that can be made by atmospheric-pressure distillation is limited by the temperature at which the feed begins to decompose thermally. Generally this upper temperature limit is around 350 °C. If further processing of the distillation residue (the residuum or “resid”) is desired, this is accomplished by vacuum distillation.

Vapors leaving the top of the distillation tower enter a condenser, where pentane and heavier compounds are condensed. The liquid may contain some dissolved propane and butane. This product is light gasoline. Because a distillation tower operates as an enormous reflux condenser, some of this liquid returns to the tower as reflux. Processing of these so-called light ends involves separating the dissolved propane and butane from

the remainder of the liquid. If necessary, propane and butane can be sweetened to remove hydrogen sulfide. The sweetened gases constitute the product known as liquefied petroleum gas, or more commonly by its initials LPG. The “debutanized” liquid undergoes a simple distillation, in a so-called stabilizing tower, to light naphtha, the C<sub>5</sub> and C<sub>6</sub> compounds, and to heavy naphtha, rich in C<sub>7</sub> and larger alkanes and in cycloalkanes. Light naphtha is used later in the refinery for blending with other process streams as part of the gasoline pool, i.e. all of the various products in the refinery that become blended to make the gasoline sold as the final, marketable product. Heavy naphtha typically would be processed further into gasoline by catalytic reforming (Chapter 14).

A perfect separation of components cannot be achieved in a single, simple fractional distillation. Consequently, each of the cuts withdrawn from the distillation tower contains some components that are undesirable or not wanted in that particular fraction. To remedy this, each product is sent directly to a sidestream stripper. These strippers are small, atmospheric-pressure distillation units that remove the more volatile components of each of the products. A given distillation cut, or sidestream product, enters the top of the stripper, and steam is fed into the bottom. The volatile components that have been stripped out of the cut return to the main distillation tower; the stripped product exits the bottom of the stripper and proceeds to other downstream refining operations. A sidestream stripper needs to handle only a single cut from the main distillation tower, so that physically the stripper itself can be shorter and smaller than the main tower. This makes it easy to locate the strippers in a vertical stack as if they were a single distillation tower; however, each one of the individual strippers operates separately and independently of the others.

### 12.3.2 Vacuum distillation

Some refineries have markets for materials having very high boiling ranges, such as lubricating oils. To distil crude oils without extremely high temperatures that would cause cracking and carbon deposition, the pressure must be reduced. This can be done by vacuum distillation (i.e. adding a vacuum tower) to the atmospheric-pressure distillation operation. In this case, resid from the atmospheric tower would be pumped to the vacuum tower, which operates at  $\approx 2\text{--}15$  kPa. The very low pressure results in a large volume of vapor. Consequently, vacuum towers may be 15 m diameter. The furnace outlet temperature for the vacuum tower would be in the range 380–450 °C. Steam is added, to suppress formation of carbonaceous solids from thermal cracking of the feed.

The overhead from the vacuum tower is gas oil. It comes off the vacuum tower at  $\approx 150$  °C; its boiling range at atmospheric pressure is 315–425 °C. Lubricating oil (“lube oil”) fractions are taken off the vacuum tower as sidestreams. Distilling some of the high-boiling materials that would be used to make lubricating oil could require pressures as low as 2–4 kPa, though it is usually possible to operate at 6–15 kPa. These cuts are taken at 250–350 °C. Vacuum tower bottoms, often called vacuum resid, serves as a source of asphalt, or can be sent to delayed coking (Chapter 16) for production of petroleum coke and light liquids. The resid temperature is kept at 350 °C, or less, to minimize thermal cracking and coke deposition.

The products of vacuum distillation depend on whether the intent is to produce lubricating oils. If so, gas oil would be processed further to make gasoline by catalytic

cracking (Chapter 14), or possibly treated to make a light grade of lubricating oil. The sidestreams constitute one or more fractions of lubricating oil. The bottoms serve as a source of asphalt. If lubricating oil is not a desired product, then there could be a simpler distillation into a single liquid fraction as feed for catalytic cracking, and a resid for asphalt production.

## 12.4 Introduction to petroleum distillation products

Oils vary widely in composition, so do not all give the same distillation products, or the same proportions of products. Further, current environmental regulations – likely only to become increasingly stringent in the future – and fuel-quality requirements for modern engines make it nearly impossible to obtain marketable material directly from distillation. Essentially everything sold from a modern refinery has passed through one or more additional refining operations downstream of distillation. Though distillation is the crucial operation in a refinery, without which not much else could happen, what distillation really does is to make materials that become feedstocks for downstream refining operations.

Some of the principal products are introduced in this section, to lead into more detailed discussions in Chapters 14–16. The long and colorful history of the worldwide petroleum industry has resulted in a variety of terms coming into usage, as well as differences in distillation cut points for various fractions. This section provides examples, without intending to be a comprehensive catalog, or to cover all the possible terminology or refining parameters.

### 12.4.1 Gasoline

Petroleum as fed to the refinery can contain dissolved light hydrocarbons that would be gases at ambient conditions, such as propane and butane. They come out of solution as the oil is heated for distillation, and come off the distillation column as part of the overhead stream. They have use both as fuel gases (LPG), and for sale to the petrochemical industry. The first distillation product that is liquid at ambient conditions is gasoline. In some parts of the world, gasoline is the most important energy source or product – excepting only electricity – that people encounter and use directly. In the United States, the market demand is such that about 50% of each barrel of petroleum fed to a refinery needs to be converted to gasoline. This situation is not the same worldwide, particularly as a result of the steady “dieselization” of the vehicle fleet. In some nations nowadays half the vehicles have diesel engines, and in a few countries, well over half.

Most oils yield, at best, no more than about 20% gasoline from distillation. The considerable gap between gasoline produced directly from distillation, called straight-run gasoline, and the demand for gasoline at the refinery gate, means that refiners face a considerable challenge to produce gasoline from other petroleum fractions. The other issue affecting straight-run gasoline, aside from there not being enough to meet market demand, is its poor combustion performance in modern engines, as indicated by a low octane rating. Thus refiners have the double problem of increasing both the quantity and the quality of gasoline during refining.

Properties and specifications of straight-run gasoline vary with the specific oil being processed and the type of distillation operation used. Generally, the boiling range of gasoline is 40–200 °C. This boiling range covers C<sub>5</sub>–C<sub>9</sub> *n*-alkanes, and lighter alkylcycloalkanes and alkylaromatics. Some heavier compounds that have appreciable vapor pressures at ≈150 °C could also be present in straight-run gasoline.

### 12.4.2 Naphtha

Material distilling between 30 and 200 °C is referred to as full-range naphtha. Typically, light naphtha is cut at 30 to 90 °C, and the remainder constitutes heavy naphtha. By far the most important use of naphtha is as a feedstock to catalytic reforming (Chapter 14) for production of high-octane gasoline. Naphtha is also subjected to thermal cracking to produce alkenes, of which ethylene is most important. Naphtha is seldom used directly as a fuel, except for applications in liquid fuel for portable stoves used for camping, and in cigarette lighters. Naphtha is a good solvent for organic materials, such as oils or grease, that do not dissolve in water. It is sometimes sold as “petroleum naphtha” as a cleaning solvent.

### 12.4.3 Kerosene

Development of the petroleum industry in the United States was driven by the need for kerosene, for use as a fuel in lamps and lanterns. The first well, drilled by Edwin Drake near Titusville, Pennsylvania, was in a location chosen for the presence of natural oil seeps, and on the basis of an analysis of the seepage oil that indicated the likelihood of high yields of kerosene from distillation. Typically, kerosene is taken as a fraction boiling between 150 and 275 °C. In some countries it is called paraffin.

Once, kerosene was a dominant product of petroleum refining. In that era, refineries consisted of little more than a distillation unit and storage tanks for the products. Gasoline was a nuisance to be got rid of. In the late nineteenth century kerosene was widely used as an illuminant in lamps. This application alone made it the most valuable product from petroleum. In the early decades of the twentieth century, especially after World War I, new factors emerged: the spread of electrification, especially into rural areas that previously depended on kerosene for illumination; and the great increase in affordability of gasoline-fueled automobiles. Gasoline became the most important petroleum product while kerosene no longer dominated. After World War II, displacement of gasoline-fueled piston-engine aircraft with jet aircraft revived a demand for kerosene. Kerosene does not enjoy its former dominance among petroleum products, and probably never will again, but it remains important, accounting for about 10% of refinery output. Nowadays most kerosene is upgraded further to produce aviation gas turbine fuels, commonly called jet fuels.

Jet fuel is a highly refined form of kerosene. Other applications utilize kerosene of lower quality. “Power kerosene,” sometimes also known as TVO, for tractor vaporizing oil, has been used as a cheap fuel for vehicles and machinery used in agriculture or industry. Kerosene used for domestic space heating, called household kerosene, must have a carefully controlled boiling range. If the boiling range is too low, vapors of the fuel building up inside the heater can explode upon ignition. This problem has occurred, for example, when household kerosene was inadvertently adulterated with

gasoline [C]. On the other hand, too high a boiling range leads to poor vaporization and inefficient combustion.

For any liquid fuel, the flash point expresses the temperature at which the vapors of that liquid will ignite when exposed to an open flame. The flash point provides an indication of safety in storage and handling the fuel; the higher the flash point, the less likely that the vapors will be ignited inadvertently. Household kerosene should have a flash point of  $\approx 50^\circ\text{C}$ . Because the combustion products from kerosene-fired space heaters or kerosene lamps are often vented directly into a room – not that this is a recommended practice – carbon monoxide, smoke, and soot are extremely undesirable products [D]. As a rule, the higher the hydrogen content of the fuel, the cleaner is the flame. Kerosenes high in alkanes are preferred, relative to naphthenic or aromatic fuels.

#### 12.4.4 Diesel fuel

Rudolf Diesel designed his engine to operate on fuels of lesser quality and lower cost than gasoline. Remarkably, one of Diesel's early predictions was that plant-derived oils would become important fuels for his engine; it took a while, but the steadily increasing importance of biodiesel is a testament to his sagacity. It is a tribute to the accomplishments of Diesel the engineer and of the diesel engine that diesel fuel is the only product whose name derives from that of the engineer who developed the engine in which it is used. Aside from using plant oils, much of the early developmental work focused on possible fuels such as coal tars or even pulverized coal [E]. Modern diesel engines operate on a "middle distillate" fuel, so called because its boiling range is intermediate between gasoline and naphtha on the one hand and high-boiling fuel oils and resids on the other. Several grades of diesel fuel are normally marketed, defined by the temperature at which 95% of the fuel has distilled. For the more volatile No. 1 diesel, the "95% over" point is  $288^\circ\text{C}$ , while for No. 2 diesel it is  $355^\circ\text{C}$ .

The higher boiling range of diesel relative to gasoline indicates that larger molecules are present in the diesel. Diesel fuel contains alkanes up to eicosane, and aromatics as large as alkylated naphthalenes. Diesel fuel has a lower API gravity than gasoline, and higher viscosity. Many diesel fuels have API gravities around  $35^\circ$ , lower than might be expected for alkanes boiling in the diesel-fuel range; for example, hexadecane has an API gravity of  $51^\circ$ . The lower API gravity relative to alkanes reflects the presence of substantial quantities of aromatics.

Marine diesels, the engines used on ships, use residual diesel oil, or marine diesel fuel. This is a heavier fuel than that used in automobiles and light trucks, with API gravity of about  $27^\circ$ .

#### 12.4.5 Fuel oils

Some fuel oils are distillation cuts; others come from resids. They are used as heat sources, for applications such as home heating, process heat in industry, or raising steam in electric generating plants. The terminology of fuel oils is not precise. Sometimes gas oil or diesel fuel are also classified as fuel oils; fuel oils are also called heating oils. Fuel oils are graded on the basis of viscosity. To achieve a desired viscosity, a resid can be blended with a distillation cut. Fuel oils are also classified by a numerical system, in which the increasing numbers imply increasing viscosity.



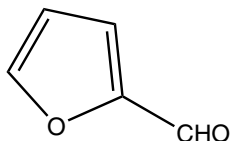
No. 1 fuel oil is comparable to kerosene. No. 2 oil is also a distillation product, very similar to No. 2 diesel fuel. The other oils are all resids (there is no No. 3 oil). The No. 5 and 6 oils are sometimes called bunker oils. They have such high viscosity that they have to be heated to be pumped through fuel lines and burner nozzles. Some bunker oils have pour points up to 30 °C, as compared with, e.g. 0 °C for marine diesel.

#### 12.4.6 Lubricating oils

Lubricating oils, or “lube oils,” have very high boiling ranges, and are usually produced by vacuum distillation. The overhead from the vacuum tower is gas oil. Lube oils are taken off as sidestreams. The vacuum bottoms are asphalt. Lube oil could consist of: 20–25% alkanes, both straight- and branched-chain; 45–50% cycloalkanes of one to three rings, possibly with alkyl side chains; 25% alkylated hydroaromatic compounds of two to four rings; and 10% high molecular weight aromatics. Lube oils might amount to  $\approx 2\%$  of the total petroleum processed, but their high selling price makes them desirable products. An enormous array of products, numbering into the thousands, is sold for lubrication applications.

Four characteristics are desirable for lube oils. High-temperature stability helps the oil resist degradation from heat generated by the friction of the parts the oil is supposed to be lubricating. Low-temperature fluidity ensures that the oil will flow between moving parts even at low temperatures, such as when starting an engine in the winter. Adhesiveness assures that the oil molecules will cling to the metal surfaces even under very high shear rates. The effect of temperature on viscosity should be minimal, so that fluidity of the oil will be nearly the same from a cold start up to high temperatures that might be generated by high-speed operation. Long-chain alkanes provide most of these properties.

If simple vacuum distillation is not adequate to provide good-quality lube oil, solvent extraction with furfural (12.1)



12.1 Furfural

dissolves aromatics, cycloalkanes, and NSOs. NSOs can be removed by clay treatment. Clay absorbs the NSOs via electrostatic interactions between the polar NSOs and the surface of the clay.

When lubricating applications call for a material of viscosity even higher than a lube oil, semi-solid lubricants called greases can be used. Usually grease is made by blending lube oil with a so-called metallic soap, a salt of fatty acids with a multivalent cation such as aluminum, calcium, or zinc.

#### 12.4.7 Waxes

Alkane molecules in waxes have 18–56 carbon atoms. Waxes are moderately hard, brittle solids at room temperature, generally melting in the range 50–60 °C. The dominant market for wax is the food industry, for impregnation of paper and cardboard for food preservation. The original market, which still exists, was manufacture of

candles. The related petrolatums are semi-solid materials at room temperature (sometimes called petroleum jelly), having a broad melting range ( $\approx 40\text{--}80^\circ\text{C}$ ). They find use in the pharmaceutical and cosmetic industries, sold under various brand names for softening and lubricating skin.

Waxes can also be useful feedstocks for the chemical industry. Thermal cracking of waxes at  $540\text{--}565^\circ\text{C}$ ,  $0.2\text{--}0.4\text{ MPa}$ , and  $5\text{--}15\text{ s}$  residence time produces 1-alkenes in the  $\text{C}_6\text{--}\text{C}_{20}$  range [F]. Wax cracking is a  $\beta$ -bond scission process. Unzipping, which involves a succession of  $\beta$ -bond scissions, produces very high yields of ethylene. Cracking for ethylene production is done at much higher temperatures ( $750\text{--}900^\circ\text{C}$ ), which increases endothermic bond breaking.

### 12.4.8 Asphalt

Asphalts are mixtures of aromatics, long-chain alkanes, and high molecular weight NSOs. Asphalts can have pour points exceeding  $95^\circ\text{C}$ . Vacuum resid provides a good source of asphalt. Treating resid with liquid propane at  $70^\circ\text{C}$  and  $3.5\text{ MPa}$  dissolves all of its components except the asphalt. Once the asphalt has been separated, reducing the pressure lets the propane evaporate, yielding a product called residual lube oil. Residual lube oil can be upgraded by an appropriate combination of solvent extraction, dewaxing, and clay treatment.

Deasphalting vacuum resid can serve different purposes. On the one hand, deasphalting can be used to make asphalt as a marketable product, such as for road paving. Alternatively, the process can be used to remove asphaltenes that would contribute to coke formation on catalysts in downstream processing of the deasphalted oil (Chapter 13).

### Notes

- [A] Native Americans used petroleum as a medicine, which might actually work for the highly paraffinic Penn-grade crudes. A product called mineral oil, liquid paraffin, or paraffin oil is available under numerous trade names and has been used as a laxative and a purgative. It is a mixture of various alkanes, probably not much different from the best-quality Penn-grade crude.
- [B] An ideal solution is one in which intermolecular interactions are completely uniform. For the famous two-component mixture *A* and *B*, this means that forces between *A* and *A* molecules, between *A* and *B* molecules, and between *B* and *B* molecules are all the same. Its importance in distillation is that the tendency of a given molecule of, say, *A* to escape from the liquid into the vapor phase is exactly the same regardless of whether that particular molecule happens to be surrounded entirely by other molecules of *A*, or surrounded by *B* molecules, or surrounded by a mixture of *A* and *B* molecules.
- [C] A tragic case resulted when a service station had underground gasoline and kerosene storage tanks connected into a common vent stack without check valves to prevent condensed vapors from running back into the tanks. Low local demand for kerosene meant that the kerosene tank was seldom refilled and often allowed to be nearly empty. Gasoline vapors condensing in the common vent ran back into the