3 Hydrocarbons

Because twenty-first century civilisation depends so much on them, just mention the word “hydrocarbons” and many people think “fuel” without knowing much more about them. Hydrocarbons are easy to recognise and define; they are compounds containing only carbon and hydrogen atoms bonded together, but there is so much more to them than that. We take for granted combustion reactions like the following:

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H = -890.7 \text{ kJ mol}^{-1} \]

A good fuel must have more than a clean and a very exothermic combustion. The activation energy must be just right; otherwise, you have materials like the boron hydrides, many of which are spontaneously flammable in air (besides giving a solid combustion product). The products of combustion have very strong C=O and O–H bonds, so a lot of energy is released when they are formed, ensuring a very exothermic reaction.

The alkanes—those hydrocarbons containing only single bonds—form a family with a general formula C\(_n\)H\(_{2n+2}\) and, with naphthenes (cycloalkanes), are the main component of natural gas and crude oil; aromatics and asphaltenes are also present. Some scientists have suggested that fossil fuels originate deep under the earth, moving upward from the mantle and that they are possibly formed by the action of thermophilic bacteria. However, most scientists accept that preserved remains of zooplankton and algae on the bottom of a sea or lake, covered with mud and sediment and exposed to high pressure and temperature over a period of millions of years, first converted to waxy kerogen (a mixture of very large organic molecules; oil shale contains a lot of kerogen). Over a further period of heating, kerogen breaks down to much smaller hydrocarbon molecules.

**Methane** (3.1) makes up 70–95% of natural gas; the remainder is small alkanes (C\(_2\)–C\(_4\)).

![Methane molecule](image)

(3.1)

Beyond natural gas, cows, sheep, and other ruminants have methanogenic bacteria in their rumen, so methane is formed in microbial fermentation of ingested feed. A cow releases up to 300 litres of flatus a day—mainly nitrogen, but with some methane content. Another source is the biogas formed by fermenting sludge and manure; methane is also generated in landfills. It is a very clean fuel, though incomplete combustion yields carbon (soot) or toxic carbon monoxide.
Because methane is a small enough molecule to fit into the spaces within the lattice structure of ice, a good deal of methane is locked up in methane clathrates in cold sediments at bottoms of the oceans; this has the potential to be a major energy reserve. As a demonstration, the methane can be burned in “flaming snowballs”. More seriously, because the global warming potential of methane is about 20 times that of CO₂ (over a 100-year time span), there is concern about the effect that release of methane could have on climate change, especially in permafrost regions like Siberia. Levels of CH₄ in the atmosphere have risen from 700 ppb in 1750 to ~1800 ppb at present.

Apart from its use as a fuel, methane is an important chemical resource. Its reaction with steam in the presence of a hot nickel catalyst affords the mixture of CO and H₂ known as “synthesis gas”—a widely used “feedstock” to make chemicals such as hydrogen, methanol, and ethanoic acid, for example.

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \]

**Petroleum** does not mean petrol; rather, it strictly means what we call crude oil, though it is often convenient to think of crude oil and natural gas together. The alkanes CH₄ to C₂H₁₀ are gases at ~20°C, though butane liquefies under slight pressure, as can be seen in “disposable” cigarette lighters. The alkanes from C₄H₁₂ upward are liquid at ~20°C. Crude oil is usually a black or dark-brown liquid (though occasionally it is yellow, red, or green) and is separated in refining by fractional distillation (Table 3.1).

Around 84% of petroleum is used as an “energy fuel”. As the best grades are exhausted, petrol increasingly has to be obtained from heavy oil and bitumen, using processes like cracking, isomerisation, and reforming to generate short-chain alkanes and cycloalkanes. Octane (3.2) is familiar in the context of octane ratings of fuels. Crude oil would make a dreadful fuel for a car; even the gasoline fraction from refining would not be good enough for high-compression petrol engines in modern cars because it would ignite too soon and not burn smoothly.

<table>
<thead>
<tr>
<th><strong>TABLE 3.1</strong></th>
<th>Fractions from Crude Oils and Their Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crude Oil</strong></td>
<td><strong>Boiling Point (b.p.)</strong></td>
</tr>
<tr>
<td>Petroleum gas</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Gasoline</td>
<td>40–100</td>
</tr>
<tr>
<td>Naphtha</td>
<td>100–150</td>
</tr>
<tr>
<td>Kerosene</td>
<td>150–200</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>200–300</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>&gt;400</td>
</tr>
<tr>
<td>Wax and grease</td>
<td>&gt;400</td>
</tr>
<tr>
<td>Bitumen</td>
<td>&gt;400</td>
</tr>
</tbody>
</table>
The octane rating of a fuel is a measure of the resistance of fuels to autoignition in internal combustion engines. Octane rating is defined by comparing the fuel with the mixture of 2,2,4-trimethylpentane (iso-octane, 3.3) and heptane, which would have the same antiknocking capacity as the fuel being tested. The octane number of the fuel is the percentage (by volume) of 2,2,4-trimethylpentane in that mixture. “Straight-chain” alkanes have relatively low octane ratings (heptane = 0), so additives are used—branched alkanes (isooctane = 100), cycloalkanes (cyclohexane = 110), and aromatic hydrocarbons (benzene = 101; toluene = 110)—so the petrol put into the car might only contain 10%–15% of straight-chain alkanes. At one time, tetraethyllead was used to improve octane ratings (see p. 105).

\[
\text{(3.2)}
\]

Diesel fuel does not have “octane ratings”; instead, cetane numbers are assigned, based on how easily a fuel ignites under compression. Cetane itself (hexadecane, C\text{16}H\text{34}) is a typical ingredient of diesel fuel and is a liquid at room temperature; octadecane (C\text{18}H\text{36}) is the first member of the alkane series to be a solid at room temperature. Longer alkanes are waxy solids; candle wax is over 90% alkanes in the range C\text{18}H\text{38} to C\text{40}H\text{82}, with C\text{20}H\text{40} most abundant. Beeswax is a mixture of compounds—mainly esters but also carboxylic acids and alkanes, principally odd-carbon unbranched alkanes with 25–31 carbons; the most abundant is C\text{27}H\text{56}.

Large alkanes are important to plants; mixtures of alkanes coat areas of the plants exposed to the outside world. Because of their nonpolar nature, they form a hydrophobic barrier that polar water molecules cannot cross; they also protect the plant against insect pests, fungi, and bacterial infection. The main alkane in apple skin is C\text{27}H\text{56}; the presence of waxy alkanes in the skin is why apples can be polished. C\text{20}H\text{40} predominates in cabbage leaves, whilst C\text{31}H\text{64} is the principal alkane on tobacco and spinach leaves.

Hydrocarbons also form a cuticular coating in insects that is largely a mixture of linear and branched alkanes, sometimes with some alkenes. Different species have their own blend; they are used for recognition in the nest, and some insects have an amazing ability to control their emissions, as in the case of the paper wasp Polistes atrinvaldularis (Chapter 6, p. 67).

Larger molecules are components of bitumen, for covering roads or waterproofing roofs. The ultimate large alkane is polyethylene, which involves chains thousands of carbon atoms long.
Naphthenes (cycloalkanes) are saturated, with only single bonds between carbons; unlike alkanes, their general formula is \( \text{C}_n \text{H}_{2n} \). Cyclohexane, \( \text{C}_6 \text{H}_{12} \), is the most important naphthene (3.4); unlike benzene, the ring is not flat.

![Cyclohexane structure](3.4)

Cyclohexane has a high octane rating (110), so it is a good petrol additive. It is widely used as a solvent, but most cyclohexane is converted into cyclohexanone or cyclohexanone-cyclohexanol mixtures, raw material to make adipic acid, and caprolactam for making nylon. The 1974 disaster at Flixborough (Lincolnshire), which killed 28 people, was at a cyclohexane plant making caprolactam.

Ethene (3.5), also known as ethylene, is the smallest alkene.

![Ethene structure](3.5)

The double bond in alkenes is stronger than the ordinary C–C single bonds in alkanes, but because it is so electron rich and thus attracts electrophiles, this makes alkenes much more reactive than alkanes. This extra reactivity makes alkenes rare in nature; ethene is an exception. At room temperature, ethene is a colourless gas with a faintly sweet smell and taste that has anaesthetic properties. Geologists have suggested that it was formed in cracking reactions in the bitumen-containing rocks under the ancient Greek shrine at Delphi and that the famous Oracle of Delphi may have been in an ethene-induced trance when she made her predictions. Industry makes ethene, which it calls ethylene, in very large amounts by cracking alkanes; it is used to make many other chemicals (Figure 3.1), such as polythene, ethanol (used as a solvent and fuel), ethylene glycol (ethane-1,2-diol) for antifreeze and some polymers,

![Chemicals made from ethene](3.1)

FIGURE 3.1 Many chemicals are made from ethene.
phenylethene (styrene monomer for polystyrene), and chloroethene (monomer for PVC), as well as ethanal, via the Wacker process.

In nature, ethene can be produced in cells from the amino acid methionine. It has an important role as a plant growth hormone. It is produced by ripening fruit and it also brings fruit to ripeness. Nowadays fruits like bananas are picked unripe, stored until they are needed for the market, and then exposed to ethene to bring them to ripeness. Similarly, if green tomatoes are placed in a plastic bag with a ripening banana, they go red. This is why a ripe fruit (which produces ethene) should not be stacked with unripe fruit—because “one rotten apple spoils the barrel”.

Isoprene (3.6) is the parent of the terpenes, but has an important life in its own right.

\[
\begin{align*}
H_2C & \equiv \text{C} \equiv CH_2 \\
H_2 & \equiv \text{C} \equiv \text{C} \equiv CH_2
\end{align*}
\]

(3.6)

Because of its two C=C bonds, isoprene (2-methyl-1,3-butadiene; \( \text{C}_5\text{H}_8 \)) is a diene, a colourless, easily vapourised (b.p. 34°C) liquid. It is the basis of the natural hydrocarbons called terpenes, which involve isoprene units joined together, head to tail, so that they contain multiples of five carbon atoms (10, 15, 20...). Isoprene itself is not directly involved in their biosynthesis, which starts with acetyl coenzyme A. Many plants make terpenes (and terpenoid derivatives) as repellents to insects.

Trees like oak emit large amounts of terpenes and even more isoprene, causing “natural” air pollution; their oxidation by atmospheric ozone, OH, and NO\(_x\) radicals affords species like aldehydes, hydroperoxides, epoxides, and organic nitrates, which generate aerosols and haze, giving enhanced scattering of shorter wavelength light and making it look blue, as with the hazes associated with the Blue Ridge Mountains of Virginia, in the United States, or the Blue Mountains of New South Wales, Australia.

Limonene, \( \text{C}_{10}\text{H}_{16} \), is one of the most familiar terpenes. It has a chiral carbon atom, and the \((R)\)-enantiomer, \(\text{D}(\text{R})\)-limonene (3.7), is found in and extracted from the rinds of citrus fruits (especially oranges) and has a citrus smell. The \((S)\)-enantiomer, \(\text{L}(\text{S})\)-limonene (3.8), has a “pine” smell. It has been suggested that these smells are due to impurities in the source from which they are extracted. Chemically, the two isomers are identical.

\[
\begin{align*}
\text{CH}_3 & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3 \\
\text{H} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3
\end{align*}
\]

(3.7)
Pinene also has the molecular formula C_{10}H_{16}, and its isomers are an important ingredient of pine resin. The presence of flammable hydrocarbons like pinene (α-pinene (3.9), β-pinene (3.10)) is the reason for pine cones and Christmas trees burning well, given the chance; it is also why forest fires involving conifers can spread fast.

Beta-carotene (C_{20}H_{30}; 3.11) is found in many plants and fruits, and it contributes to the colour of carrots. Excess consumption of carrots and other foods and drinks containing β-carotene can lead to carotenodermia, a harmless and reversible condition manifest in orange skin, especially in the palms of the hands and soles of the feet, due to carotene deposits. During World War II, the rumour was spread that the top night-fighter crews like John "Cat's Eyes" Cunningham and Jimmie Rawnsley owed their success in 1940 and 1941 to a diet especially rich in carrots, as a way of concealing the existence of the Airborne Interception Radar (AI) sets in the Beaufighter night-fighter aircraft (see p. 55).
Rubber comes from latex, which is produced by rubber trees (e.g., *Hevea brasiliensis*) as a defence against wounding by insect predators. It is designed to gum up the mouths of predators. Rubber got its name from Joseph Priestley, who called it rubber because it rubbed out pencil marks. It is a polymer (3.12) in which isoprene molecules have been joined in a *cis* configuration, which makes it stretchy.

![Chemical structure of rubber](image)

Gutta-percha, obtained in latex from other trees (such as *Palaquium gutta* and other East Asian evergreens), is the *trans*-isomer and is not elastic (gutta-percha is often used as an insulating material for cables, not to mention golf-ball coverings). Chicle, used to make chewing gum, is a polymer with both *cis* and *trans* linkages.

In 1825, Michael Faraday was the first person to identify benzene (3.13) as a by-product of the manufacture of (illuminating) gas. Although he determined its empirical formula, it was not until the 1860s that a cyclic $C_6H_6$ structure was proposed by Josef Loschmidt and August Kekulé. In 1865, Kekulé suggested a cyclic structure with alternating single and double bonds; much later (1890), he said that the cyclic structure was due to a dream of a snake seizing its own tail. It is now recognised that a cyclic structure had been suggested by Loschmidt in 1861. Not until 1929 did Kathleen Lonsdale show the benzene structure was a regular hexagon with all carbon–carbon bonds the same length. It was some time before its low reactivity was reconciled with its unsaturated nature, and the concept of six aromatic π-electrons was only understood in the 1920s.

![Chemical structures of benzene](image)

Benzene is very toxic and can cause leukaemia; it was once used as an aftershave on account of its pleasant smell. Its simple, regular structure means that benzene molecules stack together well. Thus, in contrast to benzene, which freezes at 6°C, the larger and heavier toluene has a much lower freezing point of −93°C; the methyl substituent stops the toluene molecules from packing so well in the solid state. Although it is found in small amounts in crude oil, benzene is such an important chemical that it is manufactured in large quantities by cracking and reforming reactions. It is used as an industrial solvent, as an ingredient of gasoline, and as a source of many aromatic compounds.

The readiness of benzene to undergo controlled replacement of ring hydrogen atoms in electrophilic substitution reactions leads to ethylbenzene, source of the phenylethene monomer used to make polystyrene; cumene (1-methylphenylbenzene), used to make phenol and acetone; alkylbenzene sulfonates, used in detergents; and nitrobenzene, itself the synthon for phenylamine and amine dyes.
As with benzene, **toluene** (3.14) is found in small amounts in crude oil, but most is made by reforming reactions from molecules like methylycyclohexane. Its electron donating \(-\text{CH}_3\) group makes it more reactive to electrophilic substitution than benzene as a source of other molecules, notably TNT. There is also the possibility of reactions involving the side chain (e.g., oxidation to benzaldehyde or benzoic acid). A high-octane (111) fuel additive, toluene is a widely employed solvent that is also used in adhesives; unfortunately, it can be abused by inhalation.

New cars have an unmistakable smell, caused by volatile organic compounds (VOCs) in glues, paints, vinyls, and plastics. Research has indicated worryingly high levels of hexane and of the aromatics benzene, toluene, and xylene, so it is worth keeping the windows open for the first few weeks that you drive a new car.