Composition of Oil and Gas

TU Delft

Oil and Gas

Petroleum and natural gas are mixtures of hydrocarbons. On average they consist of 85% C, 13% H, and 2 % N, S, and O (all weight %). The main components of natural hydrocarbons belong to three groups:

- Paraffins, or n-alkanes, with the general formula C_nH_{2n+2}. For n = 1 to 4 these are gases, from n = 5 to15 liquids, and above this solids (paraffin waxes). The gases methane, ethane, propane and butane form natural gas.
- Naphthenes, with the general formula C_nH_{2n}, form saturated ring compounds in which n is 5, 6 or 7. Cyclopentane and cyclohexane, are common components of crude oils, often in the methyl- form (together 2% or more of an average crude oil).
- Aromatics, generally a minor group of hydrocarbons that contain at least one benzene ring (C_6H_6) in which all carbons share the fourth bond. They are called undersaturated because they will react to add hydrogen or other elements to their rings.

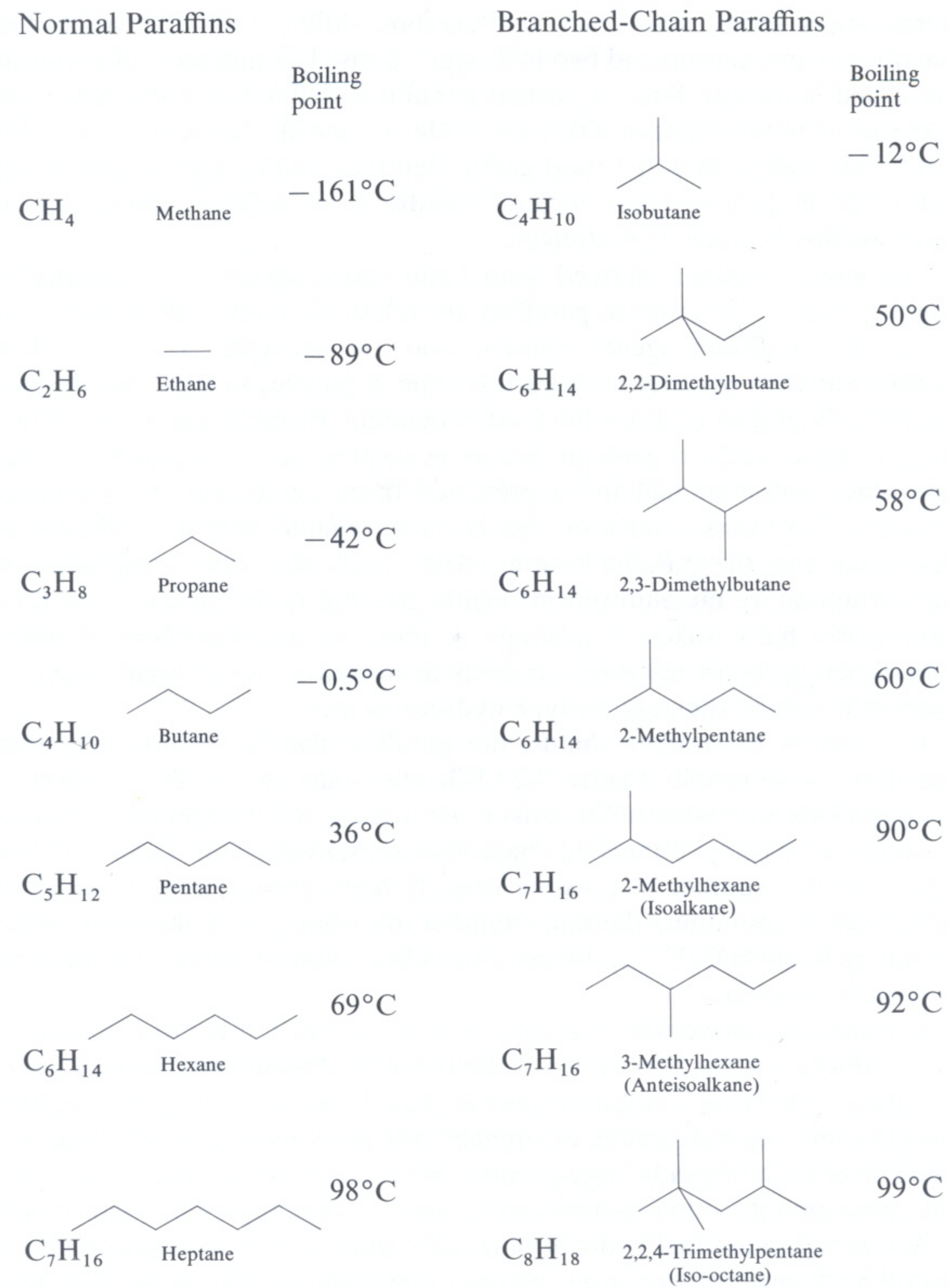
Paraffins
(normal and branched-chained)

Notice the correlation with boiling point temperatures.

Isomeres are compounds with the same chemical formula but a different molecular structure (and thus different chemical and PT properties).

Iso-octane is the standard for motor fuel ratings.

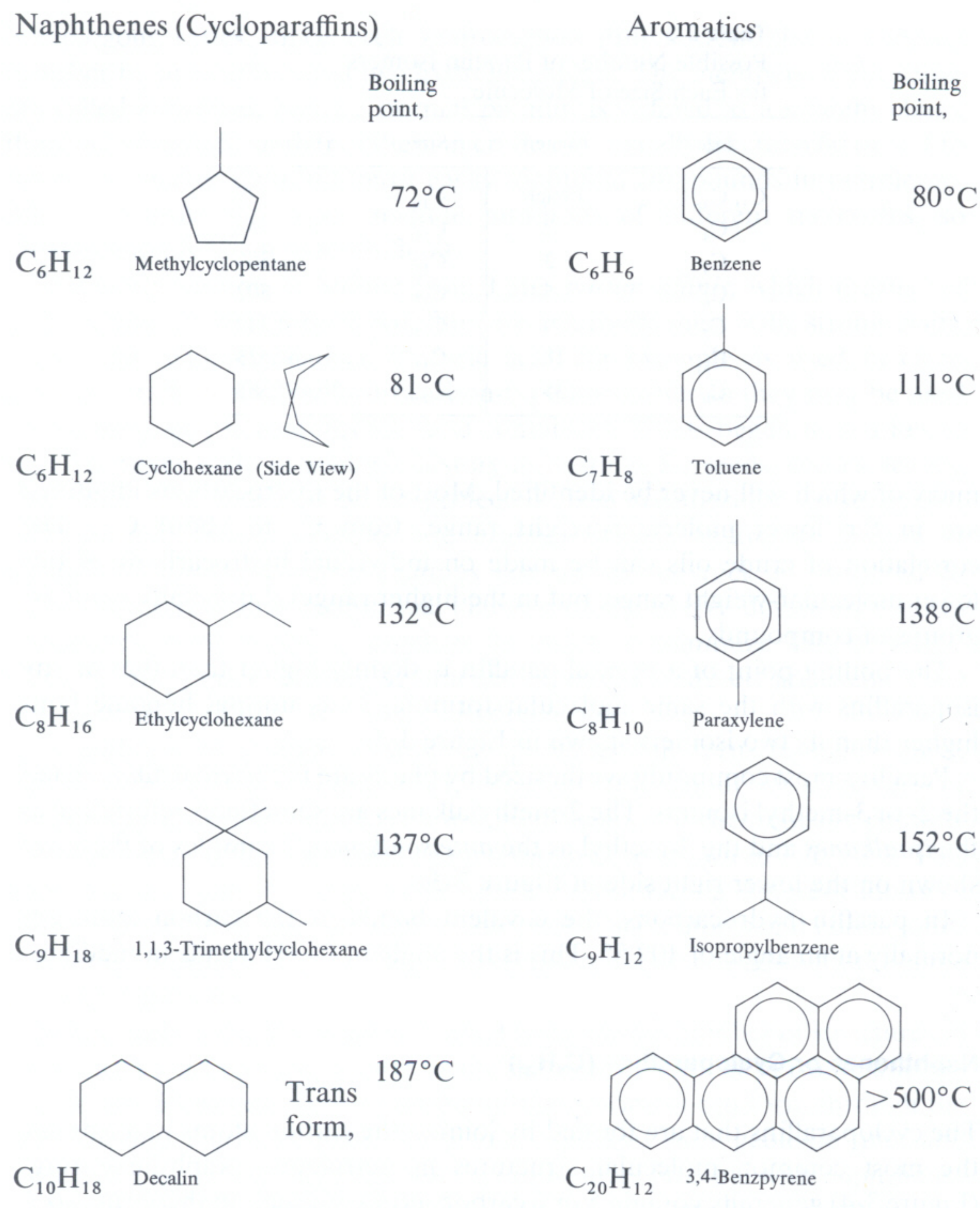
Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co



Naphthenes and Aromatics

In nature, only naphthene rings with 5 or 6 carbons occur because of the range of bond angles that carbon can have.

Aromatics all contain at least one benzene ring in which the fourth bond is shared (ring on diagram).



Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co

Aromatics

This intriguing group of hydrocarbons usually constitute less than 1% of most crude oils. Their abundance correlates inversely with oil density. Among their compounds are organic solvents like toluene and polycyclic aromatics that are carcinogenic like 3,4-benzpyrene. The more complex aromatics can range up to the size of asphaltene particles.

Aromatics are highly valued by the petrochemical industry for their large variety of uses, but because of their low abundance refineries have to synthesize them from other hydrocarbon components.

Olefin Hydrocarbons

Like aromatics these are also undersaturated hydrocarbons, but they are much more reactive. They are very common in living matter (many natural oils, vitamins A, pigments, rubber, sterols, etc.) but they do not occur in crude oils because they have been converted to more stable compounds during catagenesis. They readily reduce or polymerize to alkanes during diagenesis. Their general formulae are C_nH_{2n} and C_nH_{2n-2}. Examples: Isoprene C_5H_8, Butylene C_4H_8, Ethylene C_2H_2 .

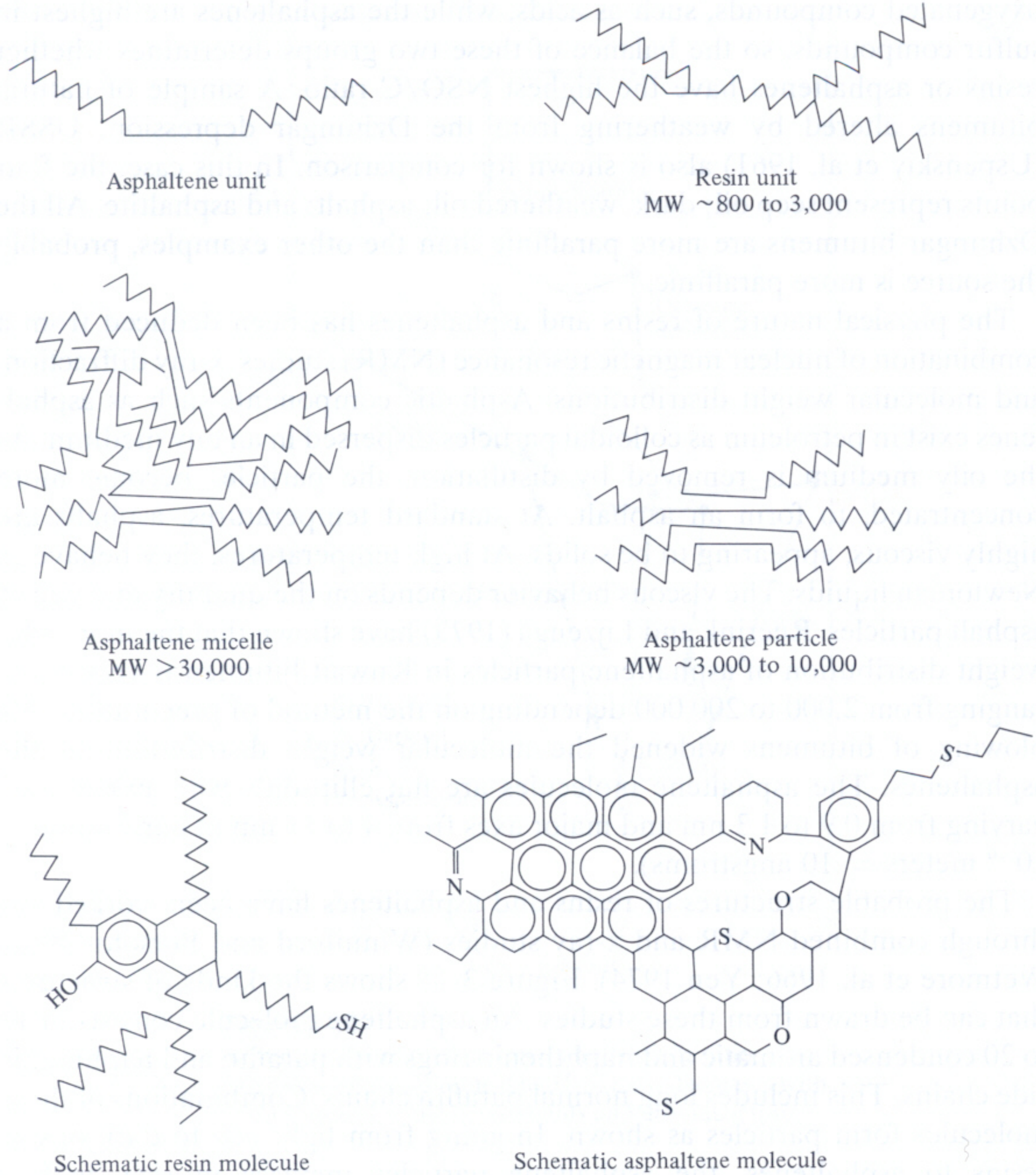
Olefin hydrocarbon can also form during the refining process of crude oil. They form the basis for the manufacturing of the explosive tri-nitrotoluole TNT.

N, S, and O Compounds

These are non-hydrocarbons but are commonly found in crude oil, particularly in the heavier oils and in residue. If they contain at least one benzene ring, they are called aromatic. If they contain at least one cycloparaffin ring (the saturated ring), they are called naphthenic. And if they have neither, they are called paraffinic. Most common, however, are combinations of these. For a examples see the next slide.

Waxes, Resins, Asphaltenes

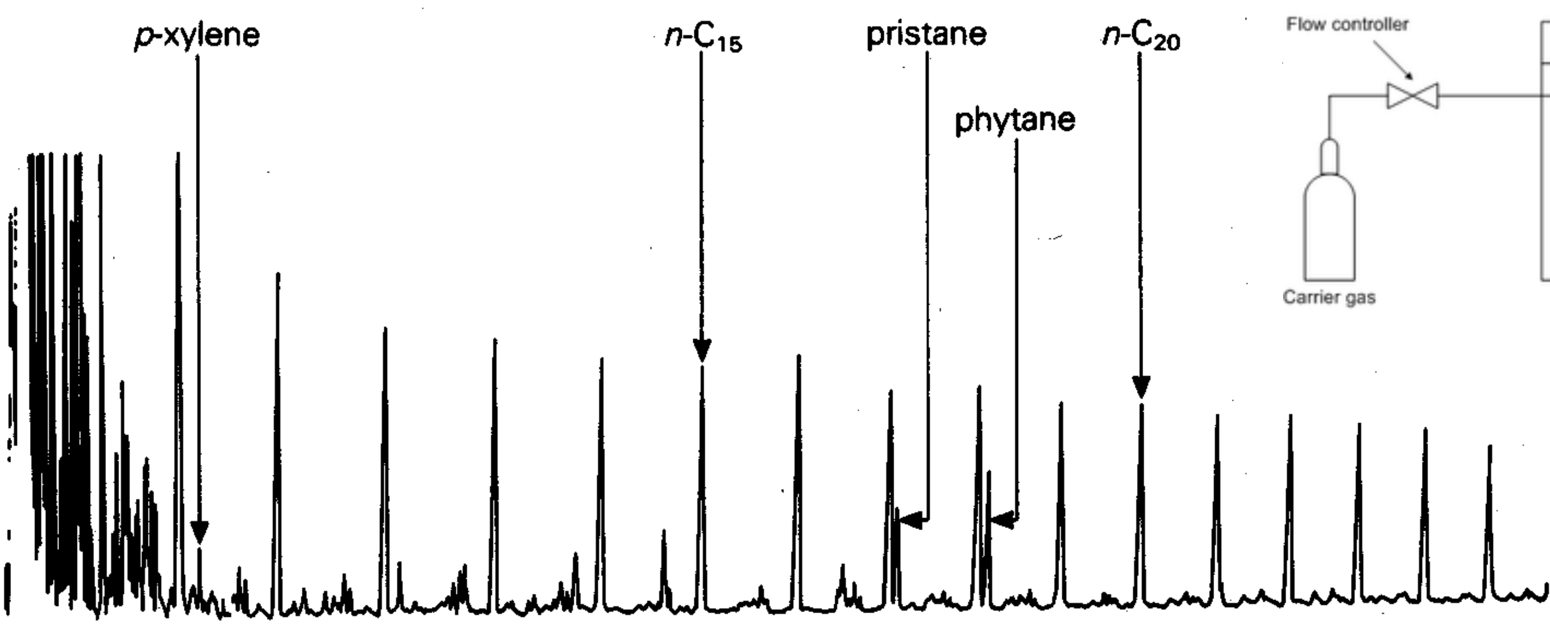
These heavier HC compounds have complex polymeric or polycyclic compositions, often with NSO incorporated. At radicals, i.e. ends with several free electrons, metallic ions can attach. This can account for high concentrations of elements such as vanadium.

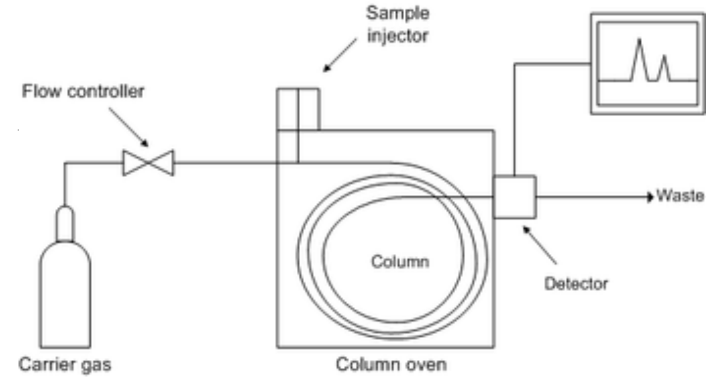


Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co

Gas Chromatography

Of course you may have wondered how petroleum compositions and structures are determined. By far the most common method is gas chromatography, which, supplemented with mass spectrometry, makes identification accurate and fast.





Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

The large peaks are paraffins, while the smaller ones belong to naphthenes. “Fingerprinting” of oils can be made by calculating the ratio of pristane over phytane.

Petro

Crude Oil Compositions

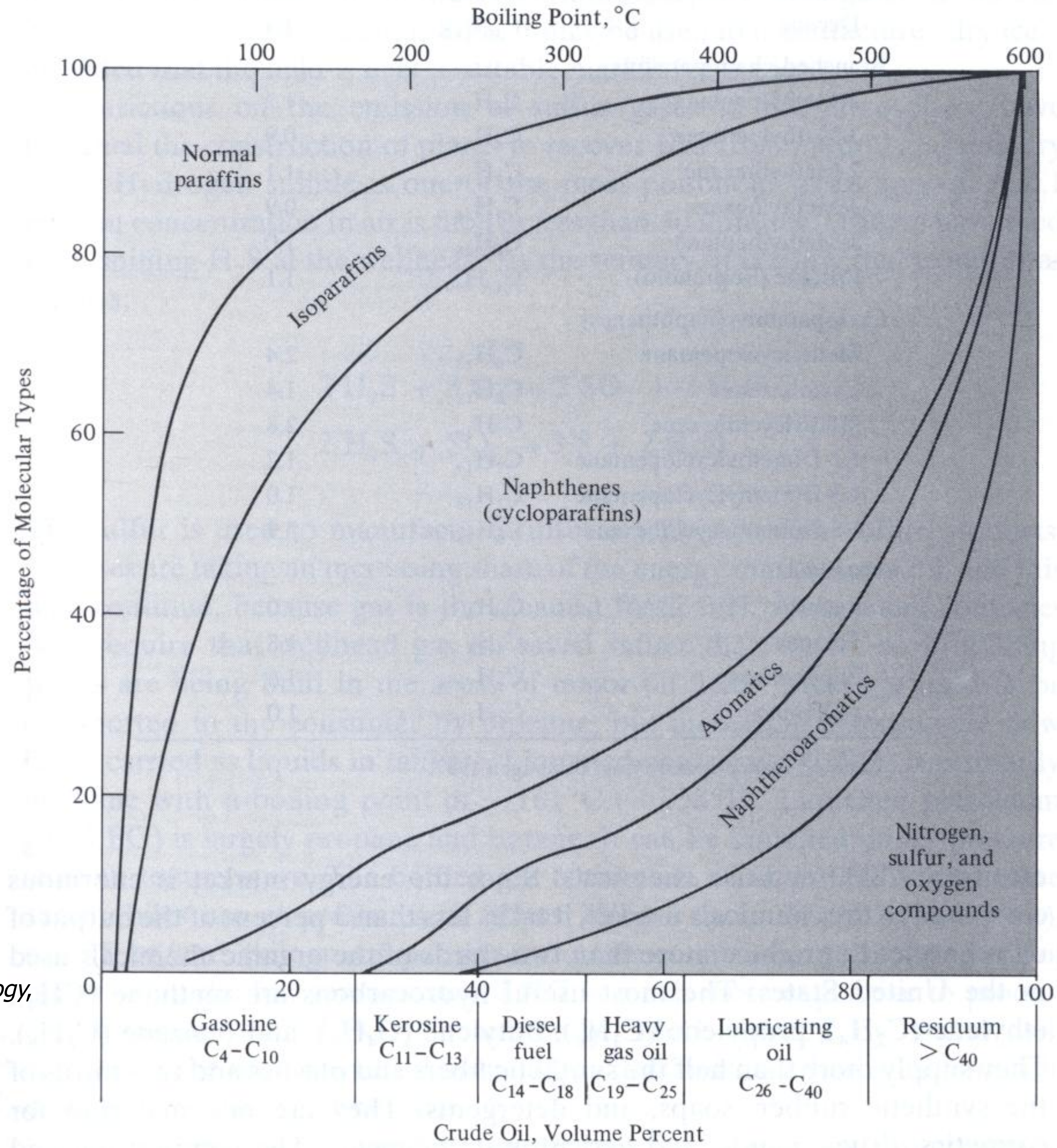
Crude oils with predominant paraffins are prized for their ease of refining but they are rare (less than 2% worldwide).

Crude oils with mostly naphtenes are called asphalt-based oils ("black oils"). They constitute about 15% of all crudes worldwide.

Most crude oils are mixed-base paraffin-naphthene, such as those from the Middle East, the North Sea, and the Mid-Continent in the US.

Most crude oils contain some hydrocarbons that do not belong to either paraffins or naphtenes, as well as NSO-nonhydrocarbons.

Chemical Composition of a Crude Oil



Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co

Distillation of Petroleum

In the distillation process, petroleum is separated into different molecular groups:

C_1-C_4:	Gas
C_5-C_{10}:	Gasoline
C_{11}-C_{13}:	Kerosine
C_{14}-C_{18}:	Diesel fuel (light gas oil)
C_{19}-C_{25}:	Heavy gas oil
C_{26}-C_{40}:	Lubricating oil
$> C_{40}$:	Residuum

These groups will be discussed briefly in the following

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Natural Gas

Natural gas usually consists mostly of methane (CH_4) but may contain variable amounts of higher-order paraffins (ethane, propane and butane). "Dry gas" is predominantly methane and ethane, while "wet gas" contains more than 50% propane and butane. Gas may originate as a byproduct during the generation of oil, from coal, or as bacterial gas (swamp gas).

Additional components in gas are CO_2, which may be used to make dry ice, and H_2S, which has to be removed because of its toxicity (0.1% is fatal to humans within 30 minutes). At the refinery, H_2S is converted into sulfur as follows:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

This process is called demercaptanization

Natural Gas ctd.

Gas is transported in pipelines, but sometimes also in liquid form on tankers. Liquefied Natural Gas (LNG) is primarily methane, while Liquefied Petroleum Gas (LPG) is largely propane and butane. The latter can be liquefied under pressure at room temperature and is cheaper to produce and transport than LNG, which has to be kept at low temperatures.

Ethylene, propylene, and butylene are gaseous olefins (see earlier) that are originally not present in petroleum but are formed in the refining process through cracking of petroleum. They are used for making plastics, rubbers, cellophane, solvents, adhesives and explosives.

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Gasoline

Notice: Americans use "gas" for gasoline

Gasoline is composed of hydrocarbons ranging from C_5 to C_{10}. Before the invention of the car with a combustion engine by Mr. Otto, there was little use for gasoline, but its demand has since completely outgrown it natural occurrence, which is between 10% and 40%.

The cracking process in the refineries was developed to produce gasoline-sized molecules from higher-order hydrocarbons. Polymerization of smaller compounds also gives gasoline molecules. Combined, these two processes can produce up to 70% gasoline from crude oil.

Niklaus August Otto, 1832-1891

Gasoline Refining

An example of cracking:

$$C_{30}H_{60} \rightarrow \underbrace{CH_4 + C_2H_4 + C_2H_6 + C_3H_6}_{\text{Gases}} + \underbrace{C_7H_8 + C_7H_{14} + C_8H_{18}}_{\text{Gasoline}}$$

An example of polymerization:

$$\underset{\text{Propylene}}{C_3H_6} + \underset{\text{Butylene}}{C_4H_8} \rightarrow \underset{\text{Heptene}}{C_7H_{14}} \xrightarrow{H_2} \underset{\text{Heptane}}{C_7H_{16}}$$

Gasoline: Use as Fuel

Untreated gasoline shows in combustion engines a phenomenon called “knocking” - actually a second, delayed explosion. To express this tendency to knock for various gasoline molecules, the first pure hydrocarbon with the greatest resistance to knocking was given a rating of 100 (2,2,4-trimethylpentane, or iso-octane), and normal heptane, which caused a considerable knock, was given a 0.

Adding an antiknock chemical, $Pb(C_2H_5)_4$ considerably reduced the knocking, but this is now phased out for environmental reasons.

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Gasoline for Other Products

One of the most useful compounds in the gasoline range is benzene, which serves as a basis for products such as insecticides, weedkillers, dyes, drugs (aspirine!), industrial solvents, plastics, nylon fibres, polyurethane foams, rubbers etc.

Benzene can be synthesized from common naphtenes such as hexane and methyl-cyclopentane with the help of a platinum catalyst.

Kerosine

The next highest group of refining products of petroleum is kerosine (also called kerosene), with molecules ranging from C_{11} to C_{13}. It is the first fraction that shows a significant amount of cyclic hydrocarbons (10-40% aromatics, also naphtenes).

Kerosine replaced whale oil for use in lamps. Its production can also be increased by cracking during the refining process. The "flash point" determines below which temperature an oil can be handled safely - i.e. without its fumes being spontaneously ignited. For kerosine, the flash point is considerably higher than for gasoline. This, together with its relatively low freezing point is a main reason for its use as airplane fuel.

Boeing 787 Dreamliner

Gas Oils

The composition of the oil fraction is complex over its total range of C_{14} to C_{25} . Paraffins are less abundant and more in the form of cyclo-paraffins. Aromatics - mostly polycyclic - as well as non-hydrocarbon compounds increase compared to kerosine.

Light gas oils are used as jet and diesel fuels. Diesel engines are compression ignition engines and work differently from combustion engines. Long-chained paraffins that knock badly are very good diesel fuels. Vice-versa, branched and cyclic hydrocarbons can be excellent gasolines but form poor diesel fuels. The quality of diesel fuel is referenced to cetane (normal hexadecane, $C_{16}H_{34}$).

Rudolf Diesel 1858-1913

Lubricating Oils and Waxes

These compounds range from about C_{26} to C_{40} , although no fixed limits exist. All types of hydrocarbons can occur here, but compared to the lighter fractions the NSO compounds significantly increase. They give these hydrocarbons their typical dark color. The amount of wax is mostly determined by straight-chain paraffins.

The pour point is defined as the temperature at which the oil does stops flowing while cooling down. Straight-chain paraffins increase the pour point, while branched-chain hydrocarbons, cyclic compounds and aromatics lower it. Waxes can be removed with solvents to lower the pour point.

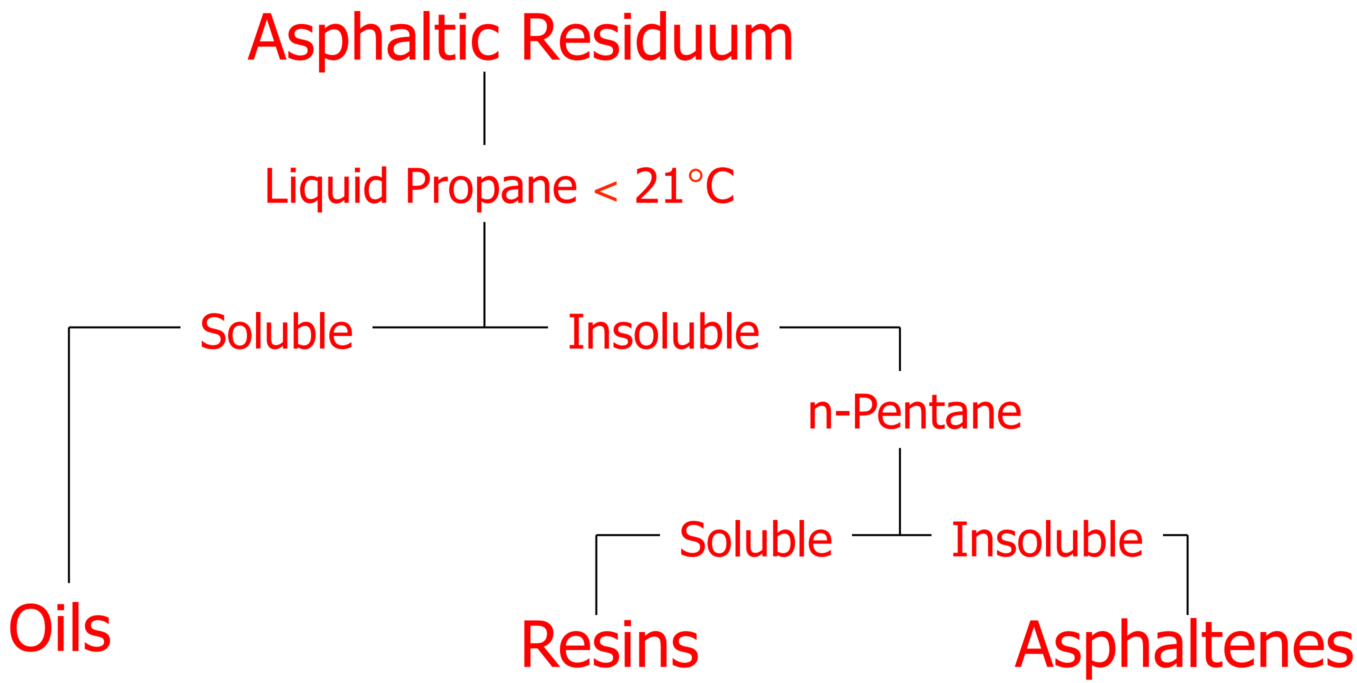
Lubricating Oils and Waxes

For a good lubricating oil, the change in viscosity with temperature is important. This is measured with the viscosity index VI, which, for an oil that does not change its viscosity, is 100. This can be the case for paraffinic oils. Aromatic oils may have very low values of VI.

Sulfur is often removed with a hydrogen treatment (see earlier chemical reactions used in demercaptanization plants)

Resins, Asphaltenes and Waxes

This is the most complex and least understood fraction of petroleum. It is the residue that remains after all lighter compounds have been distilled. The three main groups are separated from each other as follows:



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Residuum

Heavy oils, resins and asphaltenes have increasingly lower H/C ratios. The latter two often consist of heteromolecules, which are condensed aromatic and naphtene rings. Nitrogen, sulfur, and oxygen contents generally increase from heavy oil to resins and asphaltenes. The condensed aromatic structures of asphaltenes often contain free radical sites where metallic elements attach, for example vanadium (Va) or nickel (Ni). Both have a negative effect on the refining process.

Their principal use is for road construction, furnace oils, binders, filler, insulating material and adhesives. Wax is the paraffin fraction with about C_{60}. Some oils contain over 50% of these compounds. They form important resources but are not (yet) heavily produced.

The Pitch-Drop Experiment

Date	Event
1927	Experiment set up
1930	The stem was cut
December 1938	1st drop fell
February 1947	2nd drop fell
April 1954	3rd drop fell
May 1962	4th drop fell
August 1970	5th drop fell
April 1979	6th drop fell
July 1988	7th drop fell
November, 2000	8th drop fell

The experimental set-up at the University of Queensland
Viscosity is $2{\times}10^9$ P

Summary

- Petroleum has an average composition of 85% C, 13% H, and 2% N, S, and O. In natural gas, C is slightly lower and H higher.
- Distillation separates petroleum into fractions of increasingly higher complexity.
- HC types include paraffins, naphthenes, aromatics and olefins.
- Non-HC contain N,S, and O and are enriched in the heavier petroleum fractions.
- Most HC are used as fuels; only 3% are used to produce over 10,000 types of organic chemicals.
- Gas use is increasing strongly despite transportation issues.

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Study Tasks

Study HC-bearing rocks. Determine whether they are source rocks or not

Study sample oils and try to determine what types they are