

Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Industrial processes:
coal, petroleum, natural gas

Natural sources of hydrocarbons

- **Natural gas** – mixture of gaseous alkanes (C₁-C₄); methane (80-98%); depending on the field, various amounts of longer-chain alkanes, nitrogen, helium and H₂S.
- **Petroleum** – mixtures of liquid (C₅-C₁₅) alkanes (30-80%); depending on the oil field might also contain other longer (solid) or shorter (gaseous) alkanes, cycloalkanes, aromatic hydrocarbons, organic compounds with sulfur or nitrogen, organic acids, phenols, terpenes, naphthenic acids, H₂S, sulfides, polysulphides, water, inorganic salts and metalloorganic compounds.

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Natural sources of hydrocarbons

Coals are solid substances made of pressed/charred dead plant matter (effect of high temperature, pressure and limited oxygen access). The longer time and the more critical conditions organic matter went through, the more processed it became. The more processed coal is, the more coal atoms and less other atoms it consists of (decomposition products escapes as volatile compounds or crystallizes separately as inorganic compounds). However, even in the most processed coal, one can find traces of original plant structure (cells, seeds and so on).

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Natural sources of hydrocarbons

Coals are divided based on their carbon content:

- Peat (<60%, a lot of oxygen and nitrogen);
- Lignite (brown coal) (60-75%);
- Hard coal (bituminous coal, black coal) (75-95%);
- Anthracite (95-97%);

Each of the types can exhibit different structures and amount of non-carbon elements depending on the biological origin (what plants/algae were there in the first place). Time spent by the material in high temperature and pressures, oxygen access are important as well.

E.g.: polish hard coal contains (on average) 80-95% C, 4-6% H, 3-13% O, ca. 1,5% N, ca. 1% S and 3-10% inorganic salts (in fact, most of the periodic table).

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Carbon sources processing

- **Gasification: coal, oil or biomass processing method** (limited oxygen supply, high temperature, water vapor presence) into CO and H₂ gases mixture, called **syngas - synthetic gas** (as well as various content of CH₄, N₂, H₂O and CO₂).
Reaction that occurs (steam reforming):
$$\text{CH}_4 + \text{H}_2\text{O} \xrightleftharpoons{\text{cat.}} \text{CO} + 3\text{H}_2$$
(other alkanes react analogously)
$$3\text{C} + \text{H}_2\text{O} + \text{O}_2 \xrightarrow{\text{cat.}} 3\text{CO} + \text{H}_2$$
(in case of coal)
- **Syngas can be a great hydrogen source** (e.g. in fertilizers industry – ammonia), **substrate for chemical synthesis** (e.g. methanol, ethanol, alkanes – synthetic gasoline), or as a fuel itself.

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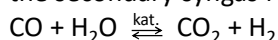
Carbon sources processing

- **Degassing: recycling of naturally occurring biogas** in waste disposal sites, spoil tips/tailings or when it is forced (e.g. through pyrolysis) from coal/oil/wood. Product of degassing is mixture of basic gases (of various content, depending on gas source): H₂, CO, CH₄, N₂, CO₂, H₂O, various organic gaseous impurities. In most cases it can be used as a fuel, e.g. coal mine gas (from degassing coal seams) or gas from spoil tips contain a lot of CH₄, wood gas contains a lot of H₂ and CO. Coke oven gas contains a lot of H₂, CH₄ and some CO.

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Natural gas processing

Raw natural gas is first purified – desulphurized, heavy hydrocarbons are removed. Purified gas is used for further applications: combustions (as a fuel), for syngas production, as a hydrogen source. For the last application it is possible to increase hydrogen content through the secondary syngas reaction with steam:



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Hard coal processing

- Coal after fragmentation and upgrading (to refined coal) by removing rocks, moisture and low-calorific components is used usually as a fuel or as a raw material for gasification.
- Hard coal can be also (if it is suitable for the application) **coked** after sorting.
- **Coking** is a **pyrolysis** process (heating up to ca. 1000°C without oxygen access), in which coal structure (legacy of the original biological material structure) is destroyed. Most carbon atoms are forming new, densely packed structures with ca. 95% carbon - **coke** (it contains impurities in form of inorganic salts, ashes)

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Hard coal processing

- By-products of coking are removed as a volatile (gaseous or decomposed to gaseous) or low melting substances. That way the coal water (H₂O, NH₃, ammonium salts), coke-oven gas (H₂, CH₄, CO) and gas pitch.
- Coal water can be used for ammonia and fertilizers production.
- Coke-oven gas can be used as a fuel (often to fire coke oven itself).
- Gas pitch is processed in a similar way as oil (fractional distillation) – is a source of aromatic compounds, phenols, pyridine derivatives (separated upon neutralization), polycyclic aromatic hydrocarbons, toluene and xylenes.

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Oil processing

Oil is degassed (petroleum gas b.p. <30°C) and dehydrated first, than processed through the **fractional distillation**, which separates oil into components/fractions (heating up to high temperature and as the mixture is cooling, successive fractions condenses) :

- gasoline (b.p. 40-180°C);
- kerosene/jet fuel (180-280°C);
- diesel oil (280-350°C);
- mazut/asphalt/residue (>350°C).

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Oil processing

- Kerosene can be used directly as a fuel to jet engines.
- Diesel oil after purification also can be used as a fuel for various vehicles (ships, trucks, cars). Long linear alkanes, main diesel oil component are combusting **explosively** (detonation/knocking), which is a normal way of combusting in diesel engines (compression-ignition). Diesel oil does not need to be enriched or refined with chemical methods (thus its price is usually lower than that of gasoline).

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Oil processing

- Gasoline, as it should combust evenly (without detonations/knocking), needs very specific structure of its components.
- **Octane number (ON)** of a compound is describing its anti-detonation properties (how much it can be compressed before detonation). Mixture of compounds has average value of its components' octane numbers. Octane number of a fuel can be increased by using additives or by processing gasoline fraction. Octane number is an empirical parameter and is compared to standards (that define ON):
n-heptane: ON = 0
2,2,4-trimethylpentane (isooctane): ON = 100

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Oil processing

- $\text{Pb}(\text{C}_2\text{H}_5)_4$ (tetraethyllead) was for years the most popular additive for ON boost. Toxic properties of lead compounds present in exhaust gas made it banned. Nowadays lead-free additives are used, like ethers and alcohols (they have ON above 100). Thus the name “unleaded” fuel.

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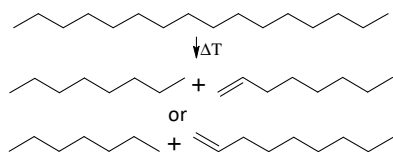
Oil processing

Enriching gasoline (increasing its average ON) can be done through **reforming** process. At high temperatures and pressures, in a presence of certain catalysts, simple/linear alkanes are converted in **isomerization** process (formation of compounds that are of the same carbon and hydrogen atoms number, but with branched carbon chains). Alternatively, compounds are subject to dehydrogenation and cyclization to cycloalkanes or even further (dehydrogenation), through aromatization, to form aromatic compounds.

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Oil processing

- **Cracking** is a process in which long linear carbon chains are breaking into shorter ones due to high temperatures (and proper catalyst), e.g.:



- **Catalytic cracking** is a process that combine cracking and reforming of its products.

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