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FUELS

WHAT IS A FUEL

A fuel (from Old French *feuaile*, from *feu* fire, ultimately from Latin *focus* fireplace, hearth) is a substance that may be burned in air (or any other oxidant-containing substance), i.e. that so quickly reacts with oxygen that heat and light is emitted in the form of a sustained flame.

Although the chemical reactions of wood in air, animal-fat in air, coal in air, natural gas in air (approximated by $\text{CH}_4/\text{O}_2/\text{N}_2$), hydrogen in oxygen (H_2/O_2), silicon in oxygen (Si/O_2), sodium in chlorine

(Na(s)/Cl₂(g)), zirconium powder in carbon dioxide (Zr/CO₂), nitrocellulose $-(C_6H_{10}O_5)_n-$ with $n=300..2000$) in any medium, etc., are all of the same chemical type (self-propagating highly-exothermic re-dox reactions, i.e. combustion processes), usually 'fuels' and 'combustion' only refer to easily flammable substances in air (the air is the oxidiser needed by a fuel to burn, and it is needed in larger quantities than fuels, so, a first glance on it seems appropriate).

THE OXIDISER

Oxygen in the air is the basic oxidant for fuels: nitrogen is basically inert, although it combines endothermically with oxygen at high temperatures to get the unwanted NO_x pollutants. The most abundant element on Earth's crust is oxygen, with 47%wt. It is also the most abundant in the hydrosphere, 86%wt. In the atmosphere, it is second to nitrogen, with 23%wt. In the whole ecosphere it is the first with 50%wt, and in the whole planet Earth it has 30%wt, only after Fe, 40%wt). Oxygen is then readily available from Earth's atmosphere; that is why it is the main oxidiser. Silicon follows as most abundant in the crust (28 %wt), but most natural Si-compounds are already fully oxidised, as sand (SiO₂) and silicate rocks (like CaO₃Si); there is no silane gas (SiH₄) free in Nature. Aluminium follows (8 %wt), but again the main Al-compounds are already fully oxidised, as bauxite (Al₂O₃) and silicates like Al₂O₃Si.

As for the fuels, hydrogen, the most abundant element of the Universe, is scarcely available in the ecosphere, mainly fully oxidised as water in the hydrosphere, where it comprises only a 3%wt, and only 0.9%wt in the whole Earth crust; the ninth most abundant element). Carbon has a poor abundance: <0.1%wt in Earth crust, and it is found basically oxidised, both in the air as CO₂, and in the rocks as CaCO₃, but there is some part un-oxidised in living and fossil matter, forming C_nH_m-compounds (hydrocarbons), which constitutes the conventional fuels.

Air is a constant-composition gas mixture, except for great variations in a minority component, water vapour, which may range from nearly 0% up to 4%, with typically 2% in volume at the Earth surface. Most combustion data for fuels refer to its burning with normal air, i.e. with 20% to 21% oxygen. Oxygen-enriched air (up to pure oxygen) accelerates combustion processes and give way to higher temperatures, whereas oxygen-depleted air may prevent combustion (usual fuels cannot be ignited if $x_{O_2} < 10\%$). Lean-oxygen air is sometimes used as oxidiser (to diminish emissions), obtained by adding to ambient air a part of the burnt gases, usually from the exhaust stream (exhaust gas recirculation, EGR), but also by letting a sizeable amount of burnt gases within the cylinder in piston engines (internal gas recirculation, IGR); in a 4-stroke engine, IGR may be just 4% but in 2-stroke engines may reach 60%.

Before Lavoisier in 1776 gave name to most chemical compounds, all gases were named as air variants (the word gas was introduced by Paracelsus around 1520 to name intangible substances). Besides normal air (21% O₂), flammable air (H₂, obtained by dripping an acid over a metal) was discovered by Priestley in 1766, fixed air (CO₂, it fixed to quicklime, CaO, to form CaCO₃, from which it was obtained with sulfuric acid) was discovered by Priestley in 1771 and found to be unable to support life or combustion, mephitic air (N₂, 'poisonous' to respiration, the residue of combustion inside a bell jar) was discovered by Rutherford in 1772 and found to be 4/5 parts of normal air, and dephlogisted air (O₂, obtained by heating HgO₂ or KClO₃) was discovered by Priestley in 1774.

WHAT IS A FUEL USED FOR

Fuels are mostly used as convenient energy stores because of their high specific energy release when burnt with omnipresent ambient air (or other specific oxidiser); the same fuel substance may be also used as a feedstock in chemical synthesis (e.g. polymers from petroleum), lubricants, paints (who has never used a coal chunk to draw), and so on, but these uses are minority. Primary fuels (natural fuels) may be difficult to find, and secondary fuels (artificial fuels) may be difficult to manufacture, but, once at hand, fuels are very easy to store, transport, and use, with the only nuisance of safety (uncontrolled combustion) and pollution (toxic emissions during storage and when burnt, dirtiness...).

Energy is a basic need to humans. Besides metabolic energy needed by any living being and supplied by the catalytic reaction of food and oxygen (some 100 W for an adult person), descendants of homo habilis need energy to change Nature to better suit their needs: to heat their home, to cook their meals, to bring potable water in (e.g. from low river courses up to their dwellings) and waste waters out, to remove the ground for aeration, to mill the grain, to turn the potter-mill, to throw weapons, for industry, for transportation of goods and people, for telecommunications, etc. Fuels, and energy in general, are used (see [Fuel consumption](#), for more details) for heat generation, for work generation, or for chemical transformations. A common problem to all human needs (except air, in most cases) is that energy is not available at the location and time we desired, and sources must be found (for energy, water, food, minerals), transportation to a better place must be arranged, as well as storage and end-use details. Storage is sometimes the most cumbersome stage, e.g. for food (all food is perishable, particularly meat and fish), and for electrical energy.

[Specific energy storage values for fuels are presented aside](#), in comparison with other energy store systems.

WHAT IS THE PROBLEM WITH FUELS?

Several:

- Fuels are dangerous, because they accumulate a lot of chemical energy that may be accidentally released, causing deathly thermal and chemical effects.
- Fuels are pollutant when burnt (and even before; most liquid fuels are cancerous); they are presently the major contribution to environmental pollution, both locally and at a global scale.
- Fuels are scarce (fossil sources are being depleted) and the sources are unevenly spread (most petroleum reserves are in the Middle East, causing economic and political instabilities).
- Fuels are difficult to handle: coal is very dirty, crude-oil is too viscous, natural gas has very low density, to say the less.

But, as just discussed, fuels are so convenient energy storage systems, that their associated problems are but to be solved. Elaborating on the above problems:

- Danger in fuel handling can be controlled and reduced to a relatively very low risk (in comparison with other accepted risks, as in transportation or sports).
- Pollution by fuels can be negligible if clean renewable fuels are used; basically a fuel is a C-H-compound that combines with oxygen to yield CO₂ (a natural compound of no harm if it does not

accumulate, as for biofuels) and H_2O (the most life-compatible compound). A short-term palliative to vehicle-engine pollution is to force a dual-fuel system (with dual fuel-reservoirs and engine controls, or even two different engines), using a non-pollutant fuel inside cities, ports and urban areas, and leaving the present more-convenient but more-pollutant fuels to highway and cruising.

- Scarcity of fuels is like scarcity of water: what we mean is scarcity of cheap good-quality sources, i.e. that we have to devote a sizeable effort within our limited capabilities. The atoms that make the fuel and oxidiser are preserved after combustion, and with the addition of some external energy (freely available from the Sun) those atoms can be arranged to form the initial fuel and oxidiser molecules. It may be difficult to think of such a new gadget added to our cars that would regenerate the gasoline and air from the exhaust gases, but think on a fuel-cell car that runs on $\text{H}_2 + (1/2)\text{O}_2 = \text{H}_2\text{O}$ and uses off-line-produced solar electricity (in the garage or at the station) to recharge the tank by electrolysis $\text{H}_2\text{O} = \text{H}_2 + (1/2)\text{O}_2$. Thus, the problem is an ancient one: it is hard to become a farmer if you can find suitable wild plants, animals and fuels.
- Water-like fuels seem the best to handle, so coal should be liquefied (i.e., converted to liquid, what is presently done by first gasifying it), crude-oil is distilled, and natural gas should be liquefied (as done with coal gases by Fischer-Tropsch process, since the 1920s). Liquid fuels are a must, particularly for vehicle propulsion (in land, water, air and space).

HYDROCARBON NOMENCLATURE

Most practical fuels are hydrocarbon mixtures (i.e. organic chemical compounds of carbon and hydrogen atoms, and maybe some additional ones); the main exception are pure carbon (C, graphite, since coal is already a mixture), and pure hydrogen (H_2). Some chemistry refreshing is appropriate here to better understand fuels:

- Hydrocarbon nomenclature:
 - By type of additional atoms. Besides the ubiquitous carbon, hydrocarbons may be: hydrogenated, oxygenated, nitrogenated, etc.
 - By type of molecular shape. chain (linear or branched), cyclic (homo- or heterocyclic).
 - By type of carbon bonding (single, double, or triple bond).
 - By mixture fraction specification (all natural fuels are mixtures):
 - From fractional distillation of raw materials (wood, coal, crude oil).
 - From chemical reforming (e.g. pyrolysis, cracking of heavy molecules, reforming by synthesis with vapour or air, like syngas).

Hydrogenated compounds may be:

- Aliphatic (oils and fats, little odour): alkanes (saturated hydrocarbons: paraffins (linear chain), isoparaffins (branched chain), and cycloparaffins or naphthenes), alkenes (ethylenes or olefins), alkynes (acetylenes).
- Aromatic (strong smell): 1-ring: benzene, phenol (-OH), toluene (- CH_3), aniline (- NH_2), nitrobenzene (- NO_2), styrene (- $\text{CH}=\text{CH}_2$); 2-rings: naphthalenes; 3-rings: anthracenes; 4-rings: tetracenes; etc...

Oxygenated compounds may be:

- Carbohydrates: $C_n(H_2O)_m$, like sugars, starch and cellulose.
- Alcohols: R-OH (phenols if R is aromatic; glycols if double OH-group, glycerols if three OH)). Methanol comes from wood distillation or natural gas reforming. Ethanol comes from biomass fermentation (directly from sugars, or after hydrolysis from starch).
- Ethers: R-O-R'. Alcohol derivatives (obtained from alcohols and isobutene, and oil derivative; in the lab, mixing alcohol and sulfuric acid); used as solvents.
- Esters: R-COO-R'. From acid+alcohol→ester+water: $R-COOH+R'-OH\rightarrow R-COO-R'+H_2O$. Volatile fragrant fats (also found on fruits and flowers).
- Aldehydes: R-CHO. Dehydrogenated alcohols. They have the divalent carbonyl group =CO. Used in the manufacture of chemicals.
- Cetones (or ketones): R-CO-R'. Volatile flammable pungent liquids, miscible with water, used in the manufacture of chemicals and as solvents.

Nitrogenated compounds may be amines (primary amines R-NH₂, secondary R-NH-R'...), amides (R-CO-NH₂), imines (R- (R'-) C=NH), imides ((R-CO)₂-N-R'), azides (RN₃), cyanates (ROCN), nitriles (R-C≡N), nitro-compounds (R-NO₂), etc.

FUEL TYPES

BY PHYSICAL STATE

Solid

As coal (mineral), charcoal (from wood) and biomass (wood, dung), but also waxes, metals and non-metals (e.g. sulfur ignites easily, producing a pungent blue flame; aluminium particles are used in the rocket boosters for heavy-lift launchers such as the Space Shuttle and Ariane 5).

Liquid

As crude-oil derivatives (gasoline, diesel, fueloil), alcohols, ethers, esters, but also LPG at low temperatures.

Notice that the usual U.S., Canadian, and New Zealand word for gasoline is simply 'gas', and that the usual British word is 'petrol'.

Gas

As natural gas, oil derivatives (LPG), acetylene, manufacture gas (from coal or oil residue) and biogas (from manure or sewage).

BY PERIOD OF NATURAL RENOVATION

Fossil fuels

Fossil fuels (coal, crude-oil and natural gas) were formed slowly (during millions of years, mainly at certain remote epochs, not uniformly; e.g. American oil was formed some 90 million years ago, whereas the rest dates from 150 million years) by high-pressure-decomposition of trapped vegetable matter during extreme global warming. Fossil fuels are found trapped in Earth's crust, up to 10 km depth, although

large pressure might stabilise them also at higher depths and temperatures (at 300 km it might be 10 GPa and 1000 °C). They are then non-renewable at humankind periods, and will eventually be commercially depleted. Notice that 'resources' refers to the total amount in Nature, whereas “reserves” refers to that portion of resources that can be economically recovered at today's selling prices, using today's technologies and under today's legislation.

Table 2. Estimated reserves and availability of fossil fuels (oil-discovery peaked in 1960s and oil-production is expected to peak around 2007; gas, some 20 years latter in both cases).

	Commercial reserve-2000	Reserve/Consumption-2000
Coal	1000·10 ¹² kg	250 yr
Crude oil	100·10 ¹² kg	40 yr
Natural gas	150·10 ¹² kg.	70 yr

Notice, by the way, that nuclear fuel reserves are also short-term: the 2·10⁹ kg present commercial reserves would last some 50 years, if only 0.5% of natural uranium is profitable used as in present nuclear plants (0.71% U-235 in natural uranium, times some 70% of burning depth of the enriched stuff, typically from 3% down to 2% U-235 in nuclear fuel rods). Two differences, however, apply to commercial reserves of nuclear fuel: first, that new breeder reactors can burn not only the U-235 fraction but the main U-238 fraction and other fissionable ores, and second, that nuclear ores have been only marginally prospected and price increments of several orders of magnitude are tolerable due to the small share of fuel price in nuclear power.

Renewable fuels

Renewable fuels (biomass) are formed in a year or a few years basis (synthetic fuels may come from fossil or from renewable sources):

- Gaseous: biogas from anaerobic fermentation or gasogen gas from pyrolysis of biomass.
- Liquid: alcohols, ethers (biopetrol), esters (biodiesel).
- Solid: wood, charcoal, fuel pellets (from wood or vegetable residues), agriculture residues, cattle manure, urban waste.

In comparison with fossil fuels, particularly with oil and gas, renewable fuels are more disperse, have less energy content, more moisture and ash content, and require more handling effort (but they are renewable).

BY PRODUCTION STAGE (RESOURCES TYPE)

Natural or primary fuels

Any commodity can be artificially produced, but it may cost a lot; humankind progress has always been based on finding raw materials that with no cost or little cost could satisfy their needs. The need for energy, to make machines work, to transport people and goods, and so on, has been met in the past and in the present by primary fuels (biofuels in the past and fossil fuels during the last two centuries).

- Fossil fuels: coal, crude oil (not used unprocessed), natural gas and biomass. They are obtained by mining (coal) or welling (oil and gas). Some pumping is usually needed. Actually, crude oil is never used as a primary fuel because there is no economy (residual crude-oil products are cheaper) and

because it is difficult to handle (being a mixture of very light and very heavy substances, its handling causes cavitation, vapour traps and sticky clogs).

- Biofuels (from biomass). They can be directly taken from nature (e.g. wood and fuel crops), or from human activity waste (agriculture residues, industrial residues, animal residues, or domestic waste).

Artificial or secondary fuels

- Distillates from natural fuels (fossil or biomass, but without chemical reaction): all petroleum derivatives, plus alcohols used as additives and mixtures, may be obtained by distilling the raw material. However, modern oil-refinery products really come from a combination of physical methods (distillation) and chemical methods (reforming and cracking).
- Reformed from natural fuels (fossil or biomass, by chemical reactions with heat, steam or partial air). They are also called synthetic fuels, and may be gaseous, liquid, or solid: hydrogen, acetylene, synthetic gasoline, synthetic oils, synthetic gases (syngas), charcoal, and coke. Synthetic liquid fuels are most promising because of their high energy density; first results date from 1897 when formaldehyde (HCHO , $T_b=98\text{ }^\circ\text{C}$) was obtained by electrical discharge on a CO/H_2 mixture (syngas), but the main milestone is the Fischer-Tropsch process of 1923, where, desulfurated syngas (generated by passing water vapour over hot coal), was made to react in presence of Fe, Ru and Co catalysts, to yield a liquid hydrocarbon blend (containing from methane to heavy waxes) from which gasoline-like and diesel-like fuels were obtained (e.g. $24\text{H}_2+12\text{CO}=\text{C}_{12}\text{H}_{24}+12\text{H}_2\text{O}$); most of South Africa's diesel fuel is currently produced this way (they also use a 50/50 Jet A-1 substitute, half from oil, half from coal). Syngas preparation is the most expensive stage in the process due to materials handling: purification of input coal, removal of sulfur, nitrogen, and ash. Methanol synthesis is another important process, as a final fuel ($\text{CO}+2\text{H}_2=\text{CH}_3\text{OH}$), or as an intermediate step to gasoline and diesel (e.g. through dehydration to dimethylether $2\text{CH}_3\text{OH}=\text{CH}_3\text{OCH}_3+\text{H}_2\text{O}$).
- Exotic fuels (not obtained from fossil or biomass fuels): hydrogen from water electrolysis, and non-hydrogen non-carbon fuels, like metals (Si, Al, Mg, Fe), used as intermediate energy stores, since they are first produced from their oxides (with cheap natural energy) and afterwards burnt to form their oxides (providing valuable artificial energy).

BY MARKETING

Non-commercial

Some biomass materials (municipal solid waste (MSW), local industrial wastes, dung), rocket propellants (e.g. black powder, hydrazine: N_2H_4), metals (Fe, Al, Mg, Si), NH_3 , etc., are considered non-commercial or special fuels. They may be directly used as fuels (burnt with air), as monopropellants (e.g. $2\text{N}_2\text{H}_4=2\text{NH}_3+\text{N}_2+\text{H}_2$), or as intermediate products; e.g. $2\text{Al}+(3/2)\text{O}_2=\text{Al}_2\text{O}_3$ is used for aluminothermy, whereas $\text{Si}+2\text{H}_2\text{O}=\text{SiO}_2+2\text{H}_2$ is used to produce hydrogen fuel ($\text{Al}+3\text{HCl}=\text{AlCl}_3+(3/2)\text{H}_2$ is only used in the lab). Ammonia is not used as a fuel because of its high auto-ignition temperature (925 K) and the difficulty of complete burning (there is NH_3 in the exhaust), but it might have a future as a hydrogen carrier since liquid NH_3 at $20\text{ }^\circ\text{C}$ ($p>854\text{ kPa}$), with $\rho=610\text{ kg/m}^3$, might yield 109 kg/m^3 of H_2 whereas the most advanced hydrogen storage systems (metal hydrides) only store 25 kg/m^3 of H_2 .

Commercial

- Coal. It was the main fuel for the Industrial Revolution in the XIX c., and still traded for domestic use during the first half of the XX c., but today it is only traded to power stations and heavy industries; mainly bituminous coal, but also lignite.
- Crude-oil derivatives (see Table 3). They were developed in parallel with the corresponding internal combustion engine during the XX c. Crude oil is not used directly as a fuel, as said before (it only burns in uncontrolled fires). Most crude-oil is now traded in relation to the spot price of certain market crudes, such as West Texas Intermediate, North Sea Brent, Dubai, or Alaskan North Slope. The spot price is the price of an individual cargo of crude traded at a particular location.
- Natural gas. It seems to be the main fuel for the immediate future. Old town gas, manufactured from coal or crude-oil, is no longer on the market.
- Special commercial fuels, like acetylene (used for cutting and welding).

Petroleum fuels

More than 50% of world's primary energy comes nowadays from petroleum, i.e. all vehicle fuels, and small and medium stationary applications fuels are petroleum derivatives, obtained by fractional distillation and reforming. Main commercial fuels and their physical data (that change according to the market requirements) are presented in Table 3.

Table 3. Main commercial fuels derivatives from crude-oil, and their main averaged properties.

	Boiling range T_b [K]	Boiling range T_b [°C]	Carbon chain range	Density (liquid at 15 °C) ρ [kg/m ³]	Viscosity at 40 °C $\nu \cdot 10^6$ [m ² /s]	Flash point T_{flash} [°C]	Main use
Liquefied petroleum gases (LPG)	<300	<30	1..4	580	0.5	-100	domestic heating, cars
Gasoline	300..500	30..200	4..12	730..760	0.5	-30	cars
Kerosene	450..650	150..350	10..14	780..850	3	40	aircrafts
Diesel	500..600	200..300	10..20	820..880	3	40	cars, lorries, boats, heaters
Fuel oil distillate	600..800	300..500	15..30	840..930	10	60	industry, ships
Fuel oil residue	>800	>500	20..40	930.1010	500	100	industry, ships. Must be heated

BY APPLICATION

For spark ignition engines

Spark ignition (SI) internal combustion engine (ICE) fuels (Otto fuels) require knock retardation (oxygenated compounds increase the octane number (RON=research-octane-number) and decrease CO and HC emissions). The reference fuel is gasoline (also named petrol, shortened to 'gas' in the USA), but some other alternative fuels exist.

- Gasoline (Eurograde-95 in UE, Premium-95 in USA).
- Propane (or better LPG), at its vapour pressure (around 1 MPa). It has good octane number (of order 100, increasing with propane content up to RON=112), and yields less emissions than

gasoline (less than a half, particularly at small loads). It is fed liquid to direct injection engines, or gaseous for carbureted engines. Most propane-fuelled-engines can work indistinctly with propane or gasoline (dual-fuel engines). LPG is a mixture of mainly propane, propylene, butane and butylenes, with composition varying widely from nearly 100% propane in cold countries, to only 20..30% propane in hot countries (e.g. 100% in UK, 50% in the Netherlands, 35% in France, 30% in Spain, 20% in Greece).

- Natural gas (mostly as a compressed gas, CNG, at 30 MPa, but sometimes in as a cryogenic liquid, LNG, at some 500 kPa). Little used in cars because of the storage, but more and more used in slave-fleet buses, power plants and cogeneration plants because it is clean at entrance and exhaust, and it has RON=130, what allows for a compression rate of 12 instead of 9, increasing the efficiency up to 40% (the engine must be specially tuned).
- Ethanol and bioethanol. Usually not pure (E100-fuel, i.e. pure ethanol, is used in Brazil) but added up to 20% to gasoline (E20-fuel or gasohol) to avoid engine changes, or nearly pure for new 'versatile fuel vehicles' (E80-fuel only has 20% gasoline, mainly as a denaturaliser). Anhydrous ethanol (<0.6% water) is required for gasoline mixtures, whereas for use-alone up to 10% water can be accepted. Bioethanol is preferentially made from cellulosic biomass materials instead of from more expensive traditional feedstock (starch crops). RON=108.
- Methanol is rarely used. Methanol is produced by steam reforming of natural gas to create a synthesis gas, which is then fed into a reactor vessel in the presence of a catalyst to produce methanol and water vapour. RON=107.
- Ethers. Usually not pure but added up to 20% to gasoline. They are better additives than alcohols because they are not so volatile, not so corrosive, and less avid for water. MTBE (methanol tertiary butyl ether, $(\text{CH}_3)_3\text{-CO-CH}_3$ or $\text{C}_5\text{H}_{12}\text{O}$), is a petroleum derivate (65% isobutene, 35% methanol), regularly added in a 10% to gasoline in EU (but there are concerns about its cancerous properties); its solubility is only 4.3%vol for fuel-in-water and 1.4%vol for water-in-fuel. A better alternative is ETBE (ethanol tertiary butyl ether, $\text{C}_6\text{H}_{14}\text{O}$), obtained by catalytic reaction of isobutene with bioethanol (with only 55% isobutene, that comes from petroleum): $\text{CH}_3\text{CH}_2\text{OH}+(\text{CH}_3\text{CH})_2=(\text{CH}_3)_3\text{-CO-CH}_2\text{CH}_3$. ETBE has lower volatility, lower water-solubility (2.3 kg/m³ at 20 °C), and higher octane number (RON=116). ETBE forms an azeotrope with ethanol (63% mol ETBE).
- Hydrogen is only used in research prototypes as a possible intermediate to future integrated hydrogen systems. RON=130.

For compression ignition engines

Compression ignition (CI) internal combustion engine (ICE) fuels (Diesel fuels) require very high injection pressure and low autoignition temperature and delay (as for cetane, $\text{C}_{16}\text{H}_{34}$, n-hexadecane, that is why it is measured as 'cetane number', defined as a cetane / methyl-naphthalene mixture which has the same ignition delay-time as the test fuel). The reference fuel is named diesel (formerly gasoil), but some other alternative fuels exist.

- Diesel oil (gasoil) from crude-oil distillation.
- Fuel oil (heavy fuel or residual oil) is only used in large marine engines.

- Natural vegetable oils (sunflower, colza, soybean) are usually not directly used because of their high viscosity (10..20 times that of diesel) and glycerine waste.
- Biodiesel (a mono-alkyl-ester mixture, obtained by transesterification of natural oils) can directly substitute diesel oil in CI engines (a mixture of 30% biodiesel and 70% fossil diesel is on the market), decreasing pollutant emissions. Biodiesel is renewable, non-toxic and biodegradable.
- Natural gas can be used as main fuel in a diesel engine if a small amount of diesel fuel is used for compression ignition (dual fuel engine). The gas is usually added by direct injection in the cylinders before ignition (to avoid high injection pressures). Hybrid solutions in which a small amount of natural gas injected in a small pre-chamber and ignited in a spark plug, provide the high temperatures needed for subsequent autoignition of the main natural gas loading, are being developed. The same approach may be used to burn other high-autoignition-temperature fuels (e.g. hydrogen) in autoignition mode (diesel mode).

Notice that a mixture of gasoline and kerosene makes no good for either the SI-engine (less octane-number) or the CI-engine (less lubrication). In case of accidental mixing, the best is to discard the mixture. The use of diesel/bioethanol mixtures in CI-engines is being investigated; up to 10% in volume of anhydrous ethanol (E10-diesel) may be burnt on unmodified CI-engines, significantly reducing particulate-matter emissions (at the expense of some reduction in cetane-number, ignition-speed and lubrication).

For gas turbine engines

As they are internal combustion engines (ICE), they cannot work with solid or heavy fuels; besides, although gas turbine engines are in principle more tolerant on fuel type than gasoline and diesel engines, high-performance gas turbine demand high-performance fuels.

- Kerosene is used for mobile applications. It has high heating value and low flash point. Aircraft jet engines currently use Jet A-1 fuel, basically 99% kerosene with 1% additives to enhance cold operations and thermal stability. The first jet engine, however, that flew in the Heinkel He 178 on 27 August 1939, used gasoline as fuel.
- Natural gas is used for stationary applications.

For boilers

- For external combustion engines (vapour turbines) and very large heaters.
 - Pulverised coal
 - Fluidised-bed coal
 - Fuel oil
- For small heaters (like domestic water heaters for space heating or for hot water)
 - Natural gas (if a network is available)
 - LPG
 - Diesel oil

For small portable applications

Fuel, which are odourless, smokeless and non-hazardous are required:

Fuels

- For lighters (portable fire sources)
 - Matches (see Pyrotechnics)
 - GLP (see SI-engines). The butane gas lighter dates back to 1933 and it is the most used today. Gas lighters are refilled by first letting the remaining gas escape (enhanced by warming up), and then connecting it to an upside-down GLP reservoir (enhanced by heating and shaking the reservoir and cooling the lighter). Keep gas lighters below 50 °C.
 - Gasoline (see SI-engines)
 - Waxed-wick fire-lighters
- For illumination
 - GLP (see SI-engines)
 - Kerosene (see SI-engines)
 - Waxes (candles)
 - Acetylene (C₂H₂, ethyne). It is used in chemical synthesis (80%) and welding (20%), and it is produced from CaC₂ and water, or by hydrocarbon cracking, or by partial oxidation of natural gas. CaC₂ was first obtained in 1892 while searching for aluminium synthesis, by passing an electric arc through calcinated limestone (CaO) and coal tar. Acetylene can be produced in situ, but it is usually traded in high-pressure bottles, in liquid form, dissolved in acetone (and stabilised within a solid porous material) since pure acetylene may decompose explosively if $p > 205$ kPa.
- For heating (cooking, plumbing, cutting)
 - GLP (see SI-engines, above). Most used at movable cooking ranges and stoves.
 - Barbecue pellets or briquettes (charcoal, pressed sawdust). BBQ-hints: (BBQ=bar-by-queue): place the charcoal in the BBQ-pan and some firelighters in the middle cavities; light it and left it for half-an-hour until the coal is ready to cook (it gets to embers covered by a fine grey ash). After cooking, the fire may be extinguished by air sophocation, and the unburnt fuel left in place ready for a new fire, or get rid of by soaking with water.
 - Acetylene (see Illumination, above). The oxy-acetylene torch is the common tool for manual cutting and welding, because of its high heating power and high combustion temperature, 3500 K, the maximum of any fuel. A typical workshop bottle of 40 litres, at 1.5 MPa, yields some 6 m³ of acetylene at room conditions (the flow rate should not be higher than 1 m³/h to avoid acetone carry-over).

For fuel cells

- Hydrogen is the nominal fuel for low temperature fuel cells, but the storage problem is not yet solved satisfactorily. Since 2004, there are city buses powered by fuel cells operating in several cities (three, with two 75 kW PEM fuel cell stacks each, in Madrid, costing some 1 200 000 € each, instead of the 200 000 € for a normal bus, roughly).
- Reformed hydrogen from other (fossil or natural) fuels (e.g. natural gas, methanol, etc.).

For pyrotechnics, propellants and explosives

(See [Pyrotechnics.pdf](#))

FUEL HISTORY

Humans must have mastered fire some 500 000 years ago (from the time of Homo Heidelbergensis). For instance, excavations at Torralba (Spain) suggest fire-hunting for elephants, wild cattle, horses, deer and woolly rhinoceroses 400 000 years ago, and the same in Anatolia 200 000 years ago. Of course, wild fires must date from the beginning of terrestrial vegetation (evidence of fire has been found in coal deposits formed 350 million years ago).

BIOMASS FUELS BEFORE THE XX C.

Most fuels used nowadays are fossil (remnant of plants that existed in the distant past), but the first fuels used by humans were from biomass (living matter used as a source of energy, notably firewood). Primitive humans must have used fire for lighting, heating, cooking, fighting, communication, religion, etc. But only non-premixed flames with condensed fuels were used up to 1850, where Bunsen mastered the premixed combustion with gaseous fuels in his famous burner.

Elementary carbon is not abundant on Earth (<0.1%wt in the crust), but it is the basic constituent of life and it is found unoxidised on all living and fossil matter. The term biomass (and biological fuels) is usually restricted to living matter (not fossilised). Since 500 000 years ago, humankind used natural carbon-compounds as their main fuel. Would it continue like that in future?, or some new kind of fuels like artificial C-compounds, H-compounds or Si-compounds will take over?

The first biofuels used were: firewood, charcoal, animal fat, animal dung, and vegetable oils. Charcoal, i.e., partially burnt wood to yield a more energetic and biological-inert fuel, was used as a paint pigment in the Palaeolithic, and as a strong fuel in metallurgy, from its earliest developments in 5000 B.C., to its take-over by coke in late XVIII c. The simple fire place was an earthy hearth surrounded by stones, later a large flat stone and since the XIX c. a flat metal plate.

Fire was a sacred element to most ancient cultures, up to Classical Greece (myth of Prometheus), and perpetual fires were maintained in front of principal temples. They used to light the flame by the sun's rays captured at the centre of a recipient called a *skaphia* (the ancestor of the parabolic mirror used today for lighting the Olympic flame).

The fireplace and the chimney

Hearths were used for lighting, heating and cooking. The first human-controlled fires might have been done out in the open where smoke presented no problem, but soon the benefit of having the fireplace protected by a shelter wall was discovered and the hearth entered the cave, with the smoke burden, perhaps the first severe anthropogenic environment pollutant (metabolic waste is not so asphyxiating). The process of smoking meats and fish might have been naturally discovered that way. Perhaps the next step was to have fireplaces in the open but surrounded by large stones that protect against gusts (and radiate heat), but when the roof was added to protect from the rain, the problem of smoke pollution and fire safety was aggravated. An opening in the roof was left to get rid of smoke and, already in recent centuries, the importance of the wall surrounding the fireplace was appreciated to the point of making a dedicated smoke tunnel: the chimney.

Chimney fireplaces have been in use at every home for heating and cooking until the middle of the XX c., and, although no longer needed because of oil and gas heaters and cooking ranges, they are still appreciated for their aesthetic and natural flavour. It must be realised, however, how embarrassing a fireplace in a modern house may be; an enclosed wood stove with glass doors on the fireplace, may be the best solution to heat with wood today; and remember that burning wet or green wood generates creosote vapours that may inflamate in the chimney (and never burn plastics, painted wood or glossy paper that generate toxic gases).

A chimney is a very effective ventilation set-up (much more than a whole in a wall), being able to remove more heat from already warm walls by air convection than the chemical heat supplied by the fuel (that is why walls extended around fireplaces to have comfort within, and not just the front side roasted and a frozen back). For the same reason, it is difficult to approach, say, 900 K, and enclosed chambers (furnaces) are required to reach higher temperatures. A chimney works on the Archimedes' principle: generating a pressure-imbalance draught, Δp , on a column of hot air of height L : $\Delta p = \Delta \rho g L$. Chimneys get coated with soot and, if not cleaned regularly, may catch fire. A chimney cap is always used to keep out the rain, leaves, and bird droppings, to inhibit downdraughts and as spark arrestor.

The chimney is a rather recent invention; the first one dated comes from an earthquake in Venice in 1347. B. Franklin in 1745 wrote some guidelines to avoid smoky chimneys, suggesting to narrow the air entrance by covering most of the front with a hanging cloth (or better a plaster wall), and to widen the flue, to keep smoke from coming out into the room. B. Thompson (Count of Rumford) in 1796 suggested to make the fireplace shallower, with widely angled side-walls, so they would radiate better, and with a streamlined flue throat with a sudden expansion to avoid smoke rebuff (it was shown by P.O. Rosin in 1932 that the sudden expansion is counterproductive). Modern fireplaces have a pre-cast iron box with a pre-cast streamlined chimney throat, which is covered with heavy refractory masonry.

Torches, oil lamps and candles

Special devices were invented to transport fire (portable burning appliances), mainly for lighting. The first portable fire was the torch, a burning branch plucked from a fire, later enhanced to a reed or tow soaked in molten fat or oil, or naturally impregnated with resin or pitch. Torches date back at least to 50 000 B.C.

Much later on, animal fat in a bowl (sea-shell or skull) with a grass wick, a kind of torch with liquid fuel pumped up by capillarity, must have been developed; the first remains were found at Lascaux famous painting cave, dating from around 20 000 B.C. Oil lamps were common in Egypt in 3000 B.C., made of clay and burning seed oil with a cotton wick. Greek lamps from 500 B.C. looked like saucers (later on with a groove) and burned olive oil in a pottery or bronze container (a modern oil lamp made of brass is shown in Fig. 1). Candles, although known before, only were in widespread since 400 B.C. The next light source, the carbon arc lamp, was not developed until the early 1800s (by Sir Humphry Davy), although it was not in widespread use until late in that century, when the incandescent carbon-filament lamp was also developed (by Thomas Edison in the 1880s). Although the carbon arc lamp is assisted by the burning of

graphite rods, electric light marked the decline of fuel lamps, which practically disappear from 1900 onwards, taking over first the traditional tungsten-filament incandescent bulb (developed in the 1920s, and being retired in the 2010s because of its low efficiency), and later by the fluorescent gas-discharge lamp (in widespread use since the 1940s, although introduced around 1900).



Fig. 1. A smoky kerosene oil-lamp.

The candle is as a kind of solid-oil lamp, tuned to feedback heat, by radiation to melt the solid fuel, made of frozen oil, semisolid fat, or wax, enhancing safety and handling (a no-spill lamp). The solid fuel melted at some 55 °C to 65 °C by radiated heat, migrating up the wick by capillary action, where it is pyrolysed at some 900 K (dark zone in the flame), generating gases that diffuse through the inner cold bulb and reach the thin combustion zone, blue at the well-ventilated bottom, yellow at the richer upper part, where products, including soot particles, are formed at some 1500 K (the hottest zone, up to 1700 K, is found off the centre on the edge of the brighter yellow portion), by reaction with outside air, whose flow is smoothly coupled to burning rate through buoyancy convection (notice that if air is artificially supplied, the candle flame flickers a lot and may be extinct, and that, in absence of a force field, as under microgravity, the candle slowly burns with a very precarious spherical blue flame).

The candle was known in Egypt (clay candle holders are found dating 3000 B.C.), but candles were not used because of the higher cost, dimmer light and higher pollution than oil lamps. Candles were made by coating a wick (the fuel pump) with pitch or animal fat. Chinese, Japanese and pre-Colombian Americans also used candles. Bee-wax candles were used by wealthy Romans as a rarity: they produce a bright flame, do not smoke, and produce a fragrant odour while burning. Candle usage widespread during the Middle Ages to light monasteries and churches; ordinary candles were made of animal fat (tallow), usually from sheep or cattle, had a dark yellowish colour and gave off a nasty smell. From the XVI c. onwards, living standards improved as evidenced by the increasing availability of candlesticks and candleholders and their appearance in households. Spermaceti candles were made of oil present in the head cavities of sperm whales; they burned with so a bright light that a spermaceti candle flame was used as a standard light measure for photometry. Since the early XIX c., candles are made of crude-oil bleached paraffins, or better of stearin, after the chemist M.E. Chevreul discovered that tallow was a mixture of two fatty acids, stearic acid and oleic acid, combined with glycerine; by removing glycerine, he achieved a harder, brighter and longer lasting wax. Candle making may be by a process of sequential dipping, or by moulding, or rolling, or extrusion, or casting.

Improvements on the wick were also achieved in mid XIX c. by weaving the cotton fibres flat and treating them with a mordant (e.g. boric acid), what causes the wick tip to stand, curl and burn, instead of just twisting the cotton fibres, what causes the fluffy wick tip to bend within the cold zone of the flame and fall into the molten wax, causing a mesh if not snuffing (cutting the charred part of the wick). If the wick would not curl and lean out of the flame and burn, it would suck too much fuel, form too much soot, and smoke. The white smoke seen when a candle is blown out, is the condensation of vaporised hydrocarbons not yet pyrolysed (it can be easily lighted).

A major development in the oil lamp took place in the 1780's when Argand, a Swiss chemist, introduced the hollow-cylinder wick, that allowed air to reach the centre of the flame, yielding a brighter flame; his assistant Quinquet added the glass chimney that bears his name (Da Vinci also sketched it). Whale oil and colza oil were most used at this time, until kerosene came into scene in mid XIX c. and finally Thomas Edison invented the incandescent light in 1879, pushing combustion illumination to the corner, but not until Coolidge's ductile wolfram replaced Edison's wretched carbon filaments (incandescent lamps have been improved by filling with gas and most recently by using a halogen gas to recycle vaporised wolfram; the fluorescent lamp was invented in 1938). Olive oil lamps made in brass have been in use in rural Spain up to mid 20th century.

Engines on biological fuels

Steam engines, the Otto engine and Diesel's engine, all started their development burning biomass fuel: wood in the boilers, alcohol in Otto's engine, and vegetable oil in Diesel's, but wood has a small heating value and was been exhausted, and liquid biofuels were too much expensive. Up to the model-T Ford, cars were designed to burn the coarse petrol distillate of the time, or alcohol (distilled from fermented sugars), or any mixture of them. But during the XX c. the petroleum industry swept all the fuel markets.

MINERAL FUELS

Mineral fuels were later discovered and only in the last three centuries massively used (up to depletion!). They are basically coal, petroleum, and natural gas. They have several advantages over biomass: fossil fuels are more concentrated, have higher energy density, lower moisture content, more constant composition, and, except for coal, less ash content. Their major drawback is being not renewable, with two direct consequences:

- They are short-term commercially available (they will be exhausted at current trends in one or two generations).
- The increase pollution, and particularly global warming, without short-term natural recycling, what means that fossil-fuel emissions must be artificially counterbalanced (e.g. by getting back excess atmospheric CO₂, which increases the greenhouse effect, and burying it in a non-pollutant way).

History of coal

Coal was known since ancient times, but only used when available on site; otherwise charcoal from wood was used.

Coal was used in China in 1100 BC, in Wales during the Bronze Age, and as a home heating fuel in England since Roman times and during the Middle Ages, but mining really started in the XVIII c., also in England, driven by the Industrial Revolution hunger to feed steam boilers. In the mid XIX c. coal also replaced charcoal in making black-powder and explosives. A great amount of coal is also used in the iron industry, its second consumer.

Around year 1880, primary world energy came from traditional biomass and coal 50%/50%, and up to mid 20th c. the tonne-coal-equivalent (1 tce=30 GJ) unit was used, later substituted by the tonne-oil-equivalent unit (1 toe=42 GJ).

History of natural condensed hydrocarbons

Natural condensed hydrocarbons (solid, sticky or liquid), generically called bitumen (Latin *bitumen* sticky) were found in Mesopotamia 5 000 years ago, and used for lighting, heating, gluing bricks together, sealing boats (Noah's Ark) and paving streets. Egyptians coated mummies and sealed pyramids with pitch. Two kind of bitumen were found: crude oil (or petroleum, Latin *petroleum* stone oil), that flows, and asphalt (Greek ασφαλτος binder) that does not flow.

Crude oil has always aroused interest as a substitute of vegetal and animal oils. In 1771 George Washington (the 1st USA President) acquired a piece of ground in what is now West Virginia because it contained an oil-and-gas spring. As demand for kerosene for illumination grew, oil well drilling started. The first success was in Titusville, Pennsylvania, where E. Drake found oil in 1859 in a 23-m deep well. Drake refined the crude oil into kerosene for lighting, and gasoline and other products made during refining were simply thrown away because people had no use for them. John D. Rockefeller enters the oil refining business in 1870 forming the Standard Oil Company (Cleveland, Ohio) to produce kerosene, for lighting purposes.

Crude-oil today is usually measured in 'toe' (metric ton oil equivalent), but in USA, the basic unit remains the 'barrel' (of 42 gallons of 231 cubic inches; there are many other barrel and gallon sizes), though there are no more old-fashioned wooden crude-oil-barrel since Drake's time except in museums (they run out of barrels, and time to fill them, just after a few years). Crude oil is always transported in bulk by tankers, pipelines, barges, and trucks. It was in 1866, seven years after Drake drilled his well, that Pennsylvania producers confirmed the 42-gallon barrel as their standard volume unit (not a real container), as opposed to, say, the 31.5 gallon wine barrel, or the 32 gallon London ale barrel, or the 36 gallon London beer barrel.

Today only fluid crude-oil is put in the market, and all of it is distilled, asphalt being the residue (more than 80% of asphalt production is used for road paving, handled at >100 °C to overcome yield stress, or lately as a water emulsion with 30%w asphalt particles about 1 μm size). The generic name for natural condensed hydrocarbons is bitumen, and, according to the fluidity, it may be crude oil (petroleum, $T_{\text{flash}} < 65$ °C, $T_{\text{pour}} < 0$ °C) or asphalt ($T_{\text{flash}} > 65$ °C, $T_{\text{pour}} > 0$ °C). They are non-crystalline highly viscous,

black or dark brown pastes, adhesive and waterproof (boat, roof and road paving), with >80%wt C and >15%wt H.

History of natural gas

Humans must have found many natural-gas sources seeping from the ground (by their hissing or bubbling, because they usually have no smell; odorants must be artificially added for safety alarm), but the ones they could not miss were the burning springs (ignited by a lightning) known as 'eternal fires' referred to in most ancient traditions (India, Persia, Greece; the most famous might be one on Mount Parnassus around 1000 B.C.).

This first well intentionally drilled to obtain natural gas was drilled in 1821 in Fredonia, New York, by William A. Hart: a 9 m deep well to enhance a surface seepage of natural gas. In the XIX c. natural gas was used locally in many USA states. Coal seams store CH₄ inside micropores, but get mixed with air in mining, releasing a 50/50 methane/air mix, unsuitable to gasoducts. It is only after 1950 that big gas pipelines (gasoducts) were built (in USA and Russia). Natural gas for transmission companies must generally meet certain pipeline quality specifications with respect to water content, hydrocarbon dew-point, heating value, and hydrogen-sulphide content.

BIOLOGICAL FUELS IN THE XXI C.

Use of biomass fuels has never been abandoned, but their importance during the Industrial Revolution fade away. A good example of this biomass back up in those days is that when Rudolph Diesel developed in 1893 his compression-ignition engine, he intended to burn coal powder (fossil), but problems with that choice (later solved with oil fuels), dictated that he demonstrated his engine at the World Exhibition in Paris in 1900 using peanut oil as fuel (biomass).

Late in the 20th c., fossil fuel depletion indicators, and local and global pollution associated to fossil fuels, have being pressing to come back from 'black fossil power' to 'green renewable power', and, as fuels continue to be the best solution for energy storage, specially for transport applications, biofuels are at the stage again.

The terms biofuels, biomass fuels and renewable fuels, may be used indistinctly if they refer to natural or artificial fuels obtained from renewable sources, although other times distinctions are introduced and then biofuels may refer to biomass derivatives directly substituting fossil fuels for the same combustor, biomass may be restricted to unprocessed biomass (forest waste, crops and agriculture waste, animal waste, domestic waste), and renewable fuel may include fuels like hydrogen obtained by electrolysis and not from biomass.

Biomass fuels have always presented several problems that might have been forgotten during the two centuries when we have profited from massive fossil fuel sources:

- Biomass-fuel sources are not found concentrated in Nature (contrary to fossil-fuel fields), and there is an inherent inefficiency in collecting them (e.g. forest wood waste, urban solid waste),

although sometimes it is compensated by the need to get rid of that matter (e.g. to prevent forest fires, to improve sanitation).

- Biomass fuels are mostly solid, and some pre-processing is needed (gasification, liquefaction) to produce fluid fuels, the kind of fuel best fitted to both engines and stationary combustors.
- Biomass fuels are less energetic than fossil fuels, because living matter is roughly a water suspension of oxygenated hydrocarbons, and fossil fuels were slowly 'cooked' over the aeons to separate water and most of the oxygen. Besides, some biomass fuels have non-fuel components that must be separated (e.g. soil in forest-waste, metals in industrial waste).
- Biomass fuels are contaminant; not contributing to global warming (because the CO₂ produced compensates with that synthesised from the air during the biomass growth), but producing much more particulates and new chemical emissions (e.g. dioxins) if not properly treated.

But the move to biofuels is not based on their short-term advantage over fossil fuels but on the long-term need to have fuels of any kind. And for the time being, living matter and their residues are a handy alternative to dying fossil fuels.

Some biofuel production methods considered are:

- Ethanol by fermentation of biomass sugars, starch or cellulose by yeast or bacteria. In Japan, a bacteria has been bred which produces ethanol from paper or rice-straw without any pre-treatment.
- Methane (actually a biogas mixture) by anaerobic digestion of biomass waste (manure, straw, sewage, municipal solid waste (MSW)).
- Oils (biodiesel) by reforming oleaginous plant seeds (e.g. colza, sunflower, soya). The marine microscopic algae *Botryococcus Braunii* has been shown to accumulate a quantity of hydrocarbons amounting to 75% of their dry weight
- Methanol from wood-waste distillation.
- Hydrogen by reforming other biofuels (e.g. ethanol or methane), or from water electrolysis by solar or wind energy (of course, this sometimes called 'solar fuel' is not bio in the sense that it has nothing to do with living matter, but what is life: a self-organised system based on water photolysis?

For mobile applications, because of higher energy density and simpler infrastructure, liquid biofuels are preferred (ethanol and biodiesel), gaseous biofuels being restricted to stationary applications.

As an aid in transition from fossil fuels to biofuels, mixtures of both are being progressively put on the market for old engines and combustors, and new engines and combustors are progressively developed to run on 'biofuel prototypes' derived from current fossil fuels (e.g. producing methanol or hydrogen from natural gas).

Another possible biofuel in the future may be hydrogen produced biologically, e.g. by a photosynthesis of hydrogen instead of carbohydrates (there are some algae that do that). Producing hydrogen by other sustainable means (direct solar energy or wind energy), however, seems closer in the future.

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