FUEL PROPERTIES

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Fuels, as for any other type of substance, can be assigned some physical and chemical properties (e.g. density, thermal capacity, vapour pressure, chemical formula, etc. However, most of the times, combustion properties are also assigned to fuels, in spite of the fact that these properties depend on the oxidiser (e.g. air, pure oxygen) and the actual process (e.g. the explosion limits depend on the boundary conditions for a given fuel/oxidiser pair). Fuel price, availability, risk, and so on, could also be considered fuel properties (attributes).

An introduction on fuels and fuel types, including some relevant properties, can be found apart in Fuels. Fuel consumption and Pyrotechnics are also covered separately. A summary table of fuel properties for normal combustion in air can also be found there. What follows is just a collection of additional notes, mainly physicochemical data, on particular fuels.

CRUDE OIL

Crude oil is not used directly as a fuel but as a feedstuff for the petrochemical factories to produce commercial fuels, synthetic rubbers, plastics, and additional chemicals. Oil refineries were originally placed near the oil fields, in part because natural gas, which could not then be economically transported long distances, was available to fuel the highly energy-intensive refining process, but since 1950, for strategic reasons crude oil was transported by tankers and oleoducts to local refineries.

Most data are highly variable with crude-oil field; typical ranges are given.

Density. Typically 900 kg/m^3 (from 700 kg/m^3 to 1000 kg/m^3 at 20 ºC; floats on water). Linear temperature variation fit. The density of spilled oil will also increase with time, as the more volatile (and less dense) components are lost, so that, after considerable evaporation, the density of some crude oils may increase enough for the oils to sink below the water surface.

Freezing and boiling points. When heating at 100 kPa a frozen crude-oil sample (from below 210 K), solid-liquid equilibrium may exist in the range 210 K to 280 K, and liquid-vapour above 280 K; vapours start to decompose at about 900 K.

Viscosity=$5\cdot10^{-6}..20\cdot10^{-6}$ m^2/s at 20 ºC. Exponential temperature variation fit. Pour point= 5..15 ºC.

Vapour pressure. 5..20 kPa at 20 ºC (40..80 kPa at 38 ºC). Vapours are heavier than air (2 to 3 times). The characteristic time for evaporation of crude-oil spills at sea is 1 day (25% in volume evaporated).

Composition. Each crude-oil field has a different composition, that can be established by a combination of gas-chromatography, fluorescence-spectroscopy and infrared-spectroscopy techniques, and that may be used, for instance, in forensic analysis of oil spills at sea (even after refining, crude-oil derivatives may be associated to their source field). Saturated hydrocarbons content is around 60%wt, aromatics 30%wt, resins 5%wt. Sulfur content is 0.5..2%wt. Heavy metals <100 ppm. Crude-oil vapours are mainly short-chain hydrocarbons (only about 10% in volume have more than 4 carbons).

Flash-point and autoignition temperature: some 230 K and 700 K approximately.

Ignition limits: lower 0.5..1%, upper 7..15%.

Organoleptic: black, brown or dark-green colour, aromatic or sulphide odour.

Solubility. <0.4%wt, due mainly to volatile compounds.

Surface tension: 0.029 N/m with its vapours, 0.023 N/m with water.

Price: for a 100 \$/barrel (very variable), with 159 L/barrel it is 0.63 \$/L, and with 900 kg/m^3 and 42 GJ/toe, it is 16.6 \$/GJ.

GASOLINE

Types. In EU: Eurosuper-95, Eurosuper-98 (both lead-free). In the USA: Regular (97 RON) and Premium (95 RON).

Density=750 kg/m^3 (from 720 kg/m^3 to 760 kg/m^3 at 20 ºC). Thermal expansion coefficient=$900\cdot10^{-6}$ K^{-1} (automatic temperature compensation for volume metered fuels is mandatory in some countries).

Boiling and solidification points. Not well defined because they are mixtures. (e.g. when heating a previously subcooled sample at constant standard pressure, some 10% in weight of gasoline is in the vapour state at 300 K, and some 90% when at 440 K).

Viscosity=$0.5\cdot10^{-6}$ m^2/s at 20 ºC.

Vapour pressure. 50..90 kPa at 20 ºC, typically 70 kPa at 20 ºC.

Heating value. Average Eurosuper values are: HHV=45.7 MJ/kg, LHV=42.9 MJ/kg.

Theoretical air/fuel ratio: A=14.5 kg air by kg fuel.

Octane number (RON)=92..98. This is a measure of autoignition resistance in a spark-ignition engine, being the volume percentage of iso-octane in a iso-octane / n-heptane mixture having the same anti-knocking characteristic when tested in a variable-compression-ratio engine.

Cetane number=5..20, meaning that gasoline has a relative large time-lag between injection in hot air and autoignition, although this is irrelevant in typical gasoline applications (spark ignition).

Composition. Gasoline composition has changed in parallel with SI-engine development. Lead tetraethyl, $Pb(C_2H_5)_4$, a colourless oily insoluble liquid, was used as an additive from 1950 to 1995, in some 0.1 grams of lead per litre, to prevent knocking; sulfur was removed at that time because it inhibited the octane-enhancing effect of the tetraethyl lead. Its typical hydrocarbon composition is presented in Table 1. Average molar mass is M=0.099 kg/mol, and ultimate analysis (by weight; see coal analysis below for more details): 87%C and 13%H (corresponds roughly to $C_{7.2}H_{12.6}$).

Table 1. Gasoline composition*.

60% saturated (4..8 -C-)	15% lineal (n-)	best combustion, low RON
(is increasing)	30% branched (iso-)	high RON
	15% cycle	
40% unsaturated (5..9 -C-)	5% olefins (alkenes)	bad smell
(is decreasing)	35% aromatics (benzenes)	toxic, yield soot, high RON
<500 ppm Sulfur in 2000		
<100 ppm Sulfur for 2005		

*A sample showed 21% cycle-hexane, 17% iso-octane, 16% iso-pentane, 16% ethyl-bencene, 15% toluene, 12% n-decane, 3% naphthalene, and all other <1%.

Solubility in water depends on the actual compounds: hydrocarbons are very insoluble in water, but alcohols readily mix. Table 2 presents some data.

Table 2. Solubility data at 25 ºC of some gasoline compounds.

Substance	Solubility of substance in water	Water solubility in substance
ethanol (& methanol)	100%wt	100%wt
benzene	0.18%wt	0.06%wt
cyclohexane	0.006%wt	0.01%wt
iso-octane	0.0003%wt	0.006%wt

Price. In Europe in 2013, about 1.5 €/L, with variations of ±30% amongst countries (in USA some 1 €/L). In Europe, in % of retail price, the price structure is roughly: refinery output 20, transport 1, station benefit 6, special fuel tax 60, value added tax 13.

Bioethanol and ETBE

Bioethanol is bio-fuel substitute of gasoline; i.e. it is ethanol obtained from biomass (not from fossil fuels), and used as a gasoline blend.

Pure bioethanol (E100-fuel) is by far the most produced biofuel, mainly in Brazil and USA. More widespread practice has been to add up to 20% to gasoline by volume (E20-fuel or gasohol) to avoid the need of engine modifications. Nearly pure bioethanol is used 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.

ETBE (ethanol tertiary butyl ether, $C_6H_{14}O$, ρ=760 kg/m^3, LHV=36 MJ/kg), is a better ingredient than bioethanol because it is not so volatile, not so corrosive, and less avid for water. ETBE-15 fuel is a blend of gasoline with 15% in volume of ETBE. ETBE is obtained by catalytic reaction of bioethanol with isobutene (45%/55% in weight): $CH_3CH_2OH+(CH_3CH)_2=(CH_3)_3\text{-}CO\text{-}CH_2CH_3$. To note that isobutene comes from petroleum. The other gasoline-substitute ether, MTBE (methanol tertiary butyl ether, $(CH_3)_3\text{-}CO\text{-}CH_3$), is a full petroleum derivate (65% isobutene, 35% methanol).

Bioethanol is preferentially made from cellulosic biomass materials instead of from more expensive traditional feedstock such that starch crops (obtaining it from sugar-feedstocks is even more expensive). In Japan, a bacteria has been bred which produces ethanol from paper or rice-straw without any pre-treatment. Steps processes in ethanol production are:

- Milling (the feedstock passes through hammer mills, which grind it into a fine meal).
- Saccharification. The meal is mixed with water and an enzyme (alpha-amylase) and keept to 95 ºC to reduce bacteria levels and get a pulpy state. The mash is cooled and a secondary enzyme (gluco-amylase) added to convert the liquefied starch to fermentable sugars (dextrose).
- Fermentation. Yeast is added to the mash to ferment the sugars to ethanol and carbon dioxide (CO_2, a byproduct sold to the carbonate-beverage industry). Using a continuous process, the fermenting mash is allowed to flow, or cascade, through several fermenters until the mash is fully fermented and then leaves the final tank. In a batch fermentation process, the mash stays in one fermenter for about 48 hours before the distillation process is started.
- Distillation: The fermented mash contains about 10% ethanol, as well as all the nonfermentable solids from the feedstock and the yeast cells. The mash is pumped to the continuous flow, multicolumn distillation system where the alcohol is removed from the solids and the water. The alcohol leaves the top of the final column at 96% strength, and the residue from the base of the column is further processes into a high protein-content nutrient used for livestock feed.
- Dehydration: To get rid of the water in the azeotrope, most ethanol plants use a molecular sieve to capture the remaining water and get anhydrous ethanol (>99.8%wt pure).
- Denaturing: Fuel ethanol is denatured with a small amount (2%-5%) of some product such as gasoline, to make it unfit for human consumption.

DIESEL, KEROSENE, AND JET FUEL

Diesel fuel is any liquid fuel used in diesel engines, originally obtained from crude-oil distillation (petrodiesel), but alternatives are increasingly being developed for partial or total substitution of petrodiesel, such as biodiesel (from vegetal oils), and synthetic diesel (usually from a gas fuel coming from coal reforming or biomass, also named gas to liquid fuels, GTL). In all cases, diesel nowadays must be free of sulfur.

Kerosene is a crude-oil distillate similar to petrodiesel but with a wider-fraction distillation (see Petroleum fuels). Jet fuel is kerosene-based, with special additives (<1%). Rocket propellant RP-1 (also named Refined Petroleum) is a refined jet fuel, free of sulfur and with shorter and branched carbon-chains more resistant to thermal breakdown; it is used in rocketry usually with liquid oxygen as the oxidiser (RP1/LOX bipropellant). The tendency to change to biofuels or GTL fuels is also applicable here. Contrary to its etymology, present-day kerosene and derivatives are less waxy than diesel (i.e. less lubricant). Diesel and kerosene should not be taken as fully interchangeable fuels at present, because kerosene has no cetane-number specification and thus it may have large ignition delays (producing lots of unburnt emissions and engine rough-running by high-pressure peaks); besides, kerosene has less lubricity, and diesel-fuel less cold-start ability.

Diesel types. In EU: type A for road vehicles, B for industries (agriculture, fishing; same properties as type A, but red-coloured for different taxation), C for heating (not for engines; blue-coloured). In USA: No. 1 Distillate (Kerosene), and No. 2 Distillate (Diesel).

Density=830 kg/m^3 (780..860 kg/m^3 at 40 ºC). Thermal expansion coefficient=$800\cdot10^{-6}$ K^{-1}. 880 kg/m^3 for biodiesel (860..900 kg/m^3 at 40 ºC).

Boiling and freezing points. Not well defined because they are mixtures. In general, these fuels remain liquid down to −30 ºC (some antifreeze additives may be added to guarantee that).

Viscosity=$3\cdot10^{-6}$ m^2/s ($2.0\cdot10^{-6}$..$4.0\cdot10^{-6}$ m^2/s at 40 ºC) for diesel; $4.0\cdot10^{-6}$..$6.0\cdot10^{-6}$ m^2/s for biodiesel.

Vapour pressure=1..10 kPa at 38 ºC for diesel and JP-4, 0.5..5 kPa at 38 ºC for kerosene.

Cetane number=45 (between 40..55); 60..65 for biodiesel. This is a measure of a fuel's ignition delay; the time period between the start of injection and start of combustion (ignition) of the fuel, with larger cetane numbers having lower ignition delays. This is only of interest in compression-ignition engines, and only valid for light distillate fuels (because of the test engine; for heavy fueloil, a different burning-quality index is used, calculated from the fuel density and viscosity).

Flash-point=50 ºC typical (40 ºC minimum). In the range 310..340 K (370..430 K for biodiesel).

Heating value. HHV=47 MJ/kg, LHV=43 MJ/kg (HHV=40 MJ/kg for biodiesel).

Composition. All natural fuels are mixtures (and most synthetic fuels too). The analysis can be ultimate (i.e. mass fraction of chemical elements), or structural (mass fraction of identified molecules). The ultimate analysis of desulfurized kerosenes (<0.2% S), by weight, may yield some 84..86% C, some 13..15% H, and 1% impurities and additives. The structural analysis shows, by volume, some 66% of saturated hydrocarbons (linear and cycle chains), 30% aromatics (benzene derivatives), and 4% olefins (unsaturated hydrocarbons). From the ultimate analysis one may establish a reduced molecular formula (per unit carbon atom) of CH_n with n=1.8..2 (e.g. for 86% C and 14% H, n=(14/1)/(86/12=1.95). If the structural analysis is also considered, a mean molecular formula can be found (i.e., with whole number of atoms and typical carbon-chain-length, as $C_{11}H_{21}$, or $C_{12}H_{23}$, or $C_{12}H_{26}$, or $C_{13}H_{26}$, or $C_{14}H_{30}$; dodecene and tridecene are the most usual surrogates). Composition of biodiesel, by weight, may be: 77% C, 12% H, 11% O, 0.01% S.

Price. In Europe in 2013, diesel costs about 1.4 €/L, with variations of ±20% amongst countries (in USA some 1 €/L). In Europe, in % of retail price, the price structure is roughly: refinery output 20, transport 1, station benefit 6, special fuel tax 60, value added tax 13.

Jet fuels

Jet fuel is used for commercial (Jet A-1, Jet A, and Jet B) and military (JP-4, JP-5, JP-8...) jet propulsion; aviation gasoline (avgas) is used to power piston-engine aircraft. They are basically mixtures of kerosene and gasoline (half-&-half for JP-4, 99.5% kerosene for JP-5 and JP-8, 100% kerosene for Jet A-1), plus special additives (1..2%): corrosion inhibitor, anti-icing, anti-fouling, and anti-static compounds. Jet A-1 comprises hydrocarbon chains with 9 to 15 carbon atoms. Jet B (also named JP-4, with composition distribution from 5 to 15 carbon chains), is used in very cold weather, and in military aircraft.

Jet A-1 is the international standard jet fuel, with a freezing temperature of T_f=–50 ºC (–47 ºC as a limit); Jet A (with T_f=–40 ºC) is a low-grade Jet A-1 only and mostly used in USA; and Jet B (T_f<–50 ºC), the commercial name of JP-4, is only used in very cold climates. They all have a lower heating value of 42.8..43.6 MJ/kg. Minimum flash point is 60 ºC for JP-5, 38 ºC for Jet A-1 and JP-8 (typical value for Jet A-1 is T_{flash}=50 ºC, with a vapour pressure at this point of 1.5 kPa; 1 kPa at 38 ºC), and T_{flash}=–20 ºC for JP-4. Typical density at 15 ºC is 810 kg/m^3 for Jet A-1, and 760 kg/m^3 for Jet B. Jet fuel must withstand 150 ºC without fouling (dissolved oxygen in fuel exposed to air reacts with the hydrocarbons to form peroxides and eventually deposits after few hours); further heating leads to thermal cracking.

Jet A-1 specification is T_{flash}=49±4 ºC at 100 kPa (but it might decrease to T_{flash}=15 ºC at cruise altitude with 25 kPa). Fuel tank ullage can be inertized with nitrogen-enriched air with x_{O2}<12%. JP-4 has T_{flash}=20 ºC. Jet A-1 surrogate is 1-dodecene ($C_{12}H_{24}$, M=0.1683 kg/mol, although average molecular composition may be $C_{11.6}H_{22.3}$ (M=0.1615 kg/mol). Jet B (also named JP-4) surrogate is n-decane $C_{10}H_{22}$. Jet A-1 viscosity at 20 ºC is about $8.0\cdot10^{-6}$ m^2/s.

Price: Jet A-1 sells at some 0.8 $/L (about 20 €/GJ in terms of LHV).

Rocket propellant RP-1 fuel properties may be assumed to be the same as jet fuel properties.

Biodiesel

Biodiesel is a biomass-derived fuel, safer, cleaner, renewable, non-toxic and biodegradable direct substitute of petroleum diesel in compression-ignition engines, but more expensive. Biodiesel is a mono-alkyl-ester mixture obtained from natural oils, currently produced by a process called transesterification, where a new or used oil (sunflower, colza, soybean, or even animal fat) is first filtered, then pre-processed with alkali to remove free fatty acids, then mixed with an alcohol (usually methanol) and a catalyst (usually sodium or potassium hydroxide); the oil's triglycerides react to form esters and glycerol, Fig. 1, which are then separated from each other and purified. Usually 10% methanol (non-renewable) is added, and some 10% glycerol forms. Colza is also known as rape (RME=rape methyl ester, and REE=rape ethyl ester). Biodiesel surrogates are longer-chain hydrocarbons than petrodiesel: $C_{13}H_{28}$, $C_{14}H_{30}$, or $C_{15}H_{32}$.

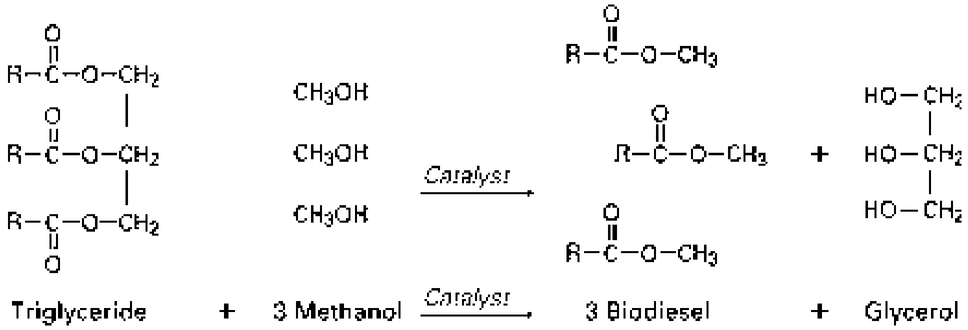

Fig. 1. Transesterification of vegetable oil to biodiesel (R is typically a 16 to 18 C-atoms hydrocarbon with 1 to 3 double bounds.

FUELOIL

Types. There are two basic types of fueloil: Distillate fueloil (lighter, thinner, better for cold-start) and Residual fueloil (heavier, thicker, more powerful, better lubrication). Often, some distillate is added to residual fueloil to get a desired viscosity. They are only used for industrial and marine applications because, although fueloil is cheaper than diesel oil, it is more difficult to handle (must be settled, pre-heated and filtered, and leave a sludge at the bottom of the tanks). Notice that, sometimes, particularly in the USA, the term 'fuel oil' also includes diesel and kerosene.

Density. Some 900..1010 kg/m^3. Varies with composition and temperature.

Viscosity. Widely variable with composition; some $1000\cdot10^{-6}$ m^2/s at 20 ºC ($4000\cdot10^{-6}$ m^2/s at 10 ºC, $(10..30)\cdot10^{-6}$ m^2/s at 100 ºC). Varies a lot with composition and temperature. Must be heated for handling (it is usually required to have $<500\cdot10^{-6}$ m^2/s for pumping and $<15\cdot10^{-6}$ m^2/s for injectors). Pour point in the range 5..10 ºC. Fueloils are usually graded by their viscosity at 50 ºC (ISO-8217).

Vapour pressure. 0.1..1 kPa at 20 ºC.

Composition. Distillate fueloils are similar to diesel oil.

Price. Typically half of crude-oil price.

Heavy fueloil

Heavy fueloil (HFO) is the residue of crude oil distillation that still flows (the quasi-solid residue is asphalt); waste oil from other industries are often added. It is the fuel used in large marine vessels because of price (about half the price of distillates). A typical HFO is IF-300 (Intermediate Fuel), which has a viscosity of $300\cdot10^{-6}$ m^2/s at 50 ºC (300 cSt), $25\cdot10^{-6}$ m^2/s at 100 ºC, ρ=990 kg/m^3 at 15 ºC, HHV=43 MJ/kg, and the flash-point at 60..80 ºC.

HFO (also named Bunker-C, or Residual fuel) may have a composition of 88%wt C, 10%wt H, 1%wt S, 0.5%wt H_2O, 0.1%wt ash, and may contain dispersed solid or semi-solid particles (asphaltenes, minerals and other leftovers from the oil source, metallic particles from the refinery equipment, and some dumped chemical wastes), plus some 0.5% water. HFO leaves a carbonaceous residue in the tanks, and may have up to 5% of sulfur (MARPOL directive is to limit it to 3.5% by 2012 and to 0.5% by 2020).

NATURAL GAS, BIOGAS, LPG AND METHANE HYDRATES

Natural gas is a flammable gaseous mixture, composed mainly of methane: 70..99% CH_4 (e.g. 70% in Libya, 99% in Alaska), 1..13% C_2H_6, 0..2% C_3H_8, and minor concentrations of H_2O, CO, CO_2, N_2, He, etc. It is found on many underground cavities, either as free deposits (e.g. Indonesia, Algeria, New Zealand) or linked to petroleum fields (e.g. Saudi Arabia, Nigeria, Alaska). Since the mid-20th century it is traded by large continental gasoducts (up to 2 m in diameter, with sensors and control valves every 25 km and pumping stations every 100 km) and LNG-ships (Liquefied Natural Gas carriers typically of 140 000 m^3 in capacity, 250 000 m^3 for new ones). The liquefaction of natural gas requires the removal of the non-hydrocarbon components of natural gas such as water, carbon dioxide and hydrogen sulfide to prevent solid plugs and corrosion.

Liquefied natural gas tankers (LNG ships) were developed in 1960s. The Algeria-Italy submarine-gasoduct started operation in 1983, and the Algeria-Morocco-Spain one in 1997. The latter gasoduct, under the Gibraltar Strait, consists of two 0.5 m in diameter welded steel pipes (tested at 16 MPa) with a concrete overcoat to protect it from anchors, 50 m apart, with 45 km undersea length up to 400 m deep (the one under Sicily Strait reaches 600 m depth). Large LNG tanks of up to 50 000 m^3 and gasholders of up to 100 000 m^3 are used as accumulators, but underground cavities (natural or artificial) seem a better solution. Before putting the dry natural gas on the market, it is sweetened (H_2S and CO_2 are removed by amine absorption), dehydrated (by glycol absorption, to avoid water freezing and hydrate formation), and some liquefying fractions are extracted (to produce 'LPG', by isentropic expansion); natural gas associated to oil fields may contain appreciable fractions of butane and heavier hydrocarbons, and it is then called 'wet gas'. Differences in natural gas composition have a sizeable impact on heating value, particularly on volume basis; e.g. HHV=36 MJ/m^3 for NG from Russia, 38 MJ/m^3 for NG from USA, 33 MJ/m^3 for NG from Netherlands, 39 MJ/m^3 for NG from UK, 42 MJ/m^3 for NG from Algeria, etc. Mind also that HHV of LNG is some 2 MJ/kg lower than natural gas, due to its low temperature.

Price of natural gas varies not only with time but among world regions (because, contrary to crude oil, transport costs are significant, and particularly if cryogenic transport is involved); in 2013, based on LHV, price is around 12 $/GJ in Europe and 4 $/GJ in USA.

Biogas is a flammable gaseous mixture, composed mainly of methane and carbon dioxide, obtained by anaerobic fermentation of condensed biomass (manure or sewage). The production may range from 20..70 m^3 of biogas per cubic metre of manure, lasting 10..30 days within a digestor (depending on the temperature, that is 20..40 ºC), where biomass is first hydrolysed by some bacteria in absence of oxygen, yielding monomers that are made to ferment by other bacteria, yielding alcohol that later turns to acetic acid and finally decomposes to methane plus carbon dioxide, the later step being the controlling stage.

LPG (liquefied petroleum gas) are petroleum derivative mixtures (gaseous at ambient temperature, but handled as liquids at their vapour pressure, 200..900 kPa), mainly constituted by propane, n-butane, iso-butane, propylene, 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. In Spain, the traditional bottle for domestic use (UD-125) holds 12.5 kg of commercial butane (56% n-butane, 25% propane, 17% iso-butane, 2% pentane, 0,1 g/kg H_2O and 1 mg/kg mercaptans, with T_b=−0.5 ºC and ρ_L=580 kg/m^3 at 20 ºC). The new aluminium bottle holds 6 kg (13 kg total, 290 mm diameter and 376 mm height). For higher rates or cold ambient, propane bottles works better. For vehicles EN-589-1993 applies. LPG is also marketed in small expandable containers for laboratory use (containing some 50..300 g of LPG, 190 g is the commonest), and portable 'camping gas' bottles (containing some 2..4 kg of LPG, 2.8 kg is commonest), with a rough molar composition of 40% propane and 60% butanes (n-butane and iso-butane).

All gaseous fuels are odourless (except those containing traces of H_2S), and odour markers (sulfur-containing chemicals, as thiols or mercaptans, e.g. ethanethiol, CH_3CH_2SH) are introduced for safety because its detection threshold for human smell is 0.4 ppm in volume).

Table 3. Data for some gaseous fuels.

	NG (Alaska)	NG (Algeria[a])	NG (North Sea)	Propane (commercial)	Butane commercial)	Biogas (typical)
ρ at 15 ºC [kg/m^3][b]	0.74	0.74	0.74	2.0 gas, 520 liquid	2.4 gas, 560 liquid[c]	1.1..1.2
HHV (LHV) [MJ/kg]	54.3 (49)	54.3 (49)	53 (48)	50 (46)	49 (45)	33 (30)
CH_4 %vol	99	89	82			60
C_2H_6 %vol		8	9			
C_3H_8 %vol		2	5	>80	<30	
C_4H_{10} %vol		1	2	<20	>70	
olefins %vol				<20	<20	
N_2 %vol		1	1			2[d]
CO_2 %vol			1			40

[a] For natural gas delivered through LNG carriers, which follows a different treatment than the one pumped through gasoducts (e.g. methane content may be as low as 83% in the latter case).

[b] Standard conditions are usually defined as 15 ºC and 100 kPa, whereas normal conditions are usually defined as 0 ºC and 101 kPa, thus one standard cubic metre equals 0.95 normal cubic metres (sometimes written 1 Sm^3=0.95 Nm^3).

[c] Thermal expansion of liquid propane $\alpha=1.5\cdot10^{-3}$ K^{-1}.

[d] Typical biogas composition: 55..65% CH_4, 35..45% CO_2, 1..4% N_2, 1..2% H_2 and <1% H_2S and H_2SO_4 before desulfuration.

Pure methane, propane and butane can be easily found from local chemicals suppliers, if the commercial mixtures traded (natural gas, commercial propane and commercial butane) are not good for some laboratory work. For small lab demonstrations they may also be obtained in situ; e.g. methane may be easily produced by means of $Al_4C_3(s)+6H_2O(l)=3CH_4(g)+2Al_2O_3(s)$, or by heating a 50/50 mix of anhydrous sodium acetate and sodium hydroxide: $NaOH(s)+NaC_2H_3O_2(s)=CH_4(g)+Na_2CO_3(s)$, as did his discoverer, the American Mathews, in 1899.

Methane hydrates are solid icy-balls (of some centimetres in size) found trapped under high pressure (>30 MPa) and chilling temperatures (0..5 ºC) in plant-covered moist places like the continental sediments on the sea floor and permafrost soil on high-latitude lands. They might be the major source of natural gas in the future; presently they are a nuisance in high-pressure gasoducts, where they may block valves. Strictly speaking, they are not hydrates (chemical compounds of a definite formula), but clathrates, i.e. an unstable network (they tend to the liquid state) of host polar molecules like water, characterized by H-bonds and regular open cavities, stabilised to a solid state by incorporating small guest non-polar molecules of appropriate size (to which they are not bonded; only van-der-Waals forces act to stabilise the network). Besides methane, carbon dioxide, hydrogen sulphide, and larger hydrocarbons such as ethane and propane, can stabilize the water lattices and form “hydrates"; smaller molecules like nitrogen, oxygen or hydrogen are much more difficult to stabilise in water.

Methane hydrates (approx. $CH_4{\cdot}6H_2O$) fizzle and evaporate quickly when depressurised, yielding some 150 times its volume of methane. Since this methane comes from very large-time biomass decomposition, the problem of global warming remains: it yields CO_2 on burning, and released CH_4 losses are worse: 20 times more relative greenhouse effect that CO_2. Hydrates soils are prone to accidental landslides, particularly during exploitation, what constitutes a high risk to extraction platforms.

HYDROGEN

In the long term, hydrogen-energy appears as the final solution to face the energy-environment dilemma of scarcity and pollution, not only for the much-pursued nuclear-fusion power stations (using hydrogen isotopes), but for the using of hydrogen as an intermediate energy carrier (like electricity), cleanly produced from water and solar energy, and cleanly converted back to water, to drive fuel cells engines and clean combustors.

Production

- Pure hydrogen (H_2) is an artificial product on Earth (1 ppm in the atmosphere), but nearly 100% of Jupiter atmosphere and 90% of all atoms in the Universe (nearly 3/4 of its total mass). On Earth, it is found combined in water, living matter and fossil matter. Discovered in 1766 by Cavendish (used in 1520 by Paracelsus as inflammable air), and named by Lavoisier in 1781 First massive production in 1782 by Jacques Charles ($Fe(s)+2HCl(aq)=FCl_2(aq)+H_2(g)$) to inflate a balloon (he flew 25 km from Paris on the same year of Montgolfier's brothers fly with a hot-air balloon). Present use is mainly for chemical synthesis (e.g. ammonia), metallurgy, ceramics, for the hydrogenation of fats, as a cryogenic fuel in rockets, in cryogenic research, and as a fuel-cell fuel.
- Production at large (world production in 2010 was $40{\cdot}10^9$ kg), is based on fossil feedstock:
  - Some 50% of world H_2 production is from natural gas reforming. The process, $CH_4+aH_2O=(2+a)H_2+bCO_2+cCO$ is carried out at 1150 K with Co-Ni catalysts, but >2000 ppm-CO is left and PEFC-type fuel cells required <20 ppm-CO. Instead of fully purifying the H_2, it is easier to purify until <1000 ppm-CO and add oxygen to get rid of the CO at the catalyst (but if more O_2 is used, it reacts with H_2 at the catalyst producing just heat). In MCFC & SOFC the CO is an additional fuel. Natural gas reforming is presently the best method to produce hydrogen while renewable sources are being developed, but availability of natural gas is in question if new major sources, as seabed clathrates, are not made available (and in that case with CO_2 sequestration).
  - Some 30% of world production is based on naphtha reforming in crude-oil refineries.
  - Another 20% of world production was based on coal reforming (declining rapidly): $C+H_2O= H_2+CO$ at 1300 K and $CO+H_2O = H_2 + CO_2$ with $Fe0\text{-}CrO_2\text{-}ThO_2$ catalyst.
  - A small percentile of world production (<4%) is based on water electrolysis from cheap hydroelectric energy in Canada and Scandinavia: $H_2O = H_2+(1/2)O_2$, with $\eta_e=0.65$. It is the purest H_2. As fossil fuels are being exhausted, water electrolysers seem to be the most popular

hydrogen sources in the future. Electrolysers with liquid potash lye produce hydrogen cheaper than other kinds of electrolysers (e.g. proton-exchange-membrane, PEM, electrolysers).

- Production at intermediate locations (for transportation or for stationary applications) by reforming (see 'Reforming' details below)
  - Methanol reforming (methanol has 12.5%wt of hydrogen).
  - Ethanol reforming (ethanol has 13%wt of hydrogen). This may be the best H_2 production method in the long term, and not electrolysis with renewable-energy.
  - Gasoline reforming (gasoline has some 16%wt of hydrogen; diesel has a little less and is not used). Gasoline may be thermally decomposed at >800 ºC (or best at 300 ºC with Ni-catalyst), $C_uH_v+uH_2O = (u+v/2)H_2+uCO$, syngas=synthesis gas, endothermic but good energy rate (78%), but contaminates a lot (and desulfurisation is required). With more $H_2O(g)$ may yield H_2+CO_2 (40%/60%). The more aromatics in gasoline, the worst reforming (that is why diesel is bad).
  - NG (natural gas, methane) or LPG (propane+butane) reforming. Methane has 25%wt of hydrogen; water only 11%, however, gaseous fuels are no good for storage and transportation. Natural gas is most used today in low-temperature fuel cells (PEFC and PAFC); it is first desulfurised (from previously added safety odorants!), then steam-reformed (yields 10% CO), afterwards shift-converted (reduces CO to 1%), and (only for PEFC) finally selectively oxidised (to <10 ppm CO).
  - Coal reforming. No good because of pollution and high temperature work.
  - From other intermediate storage compounds (too expensive at present): NH_3 (liquid at 1 MPa & 298 K, but it is a poison), N_2H_4 (flammable liquid).
- Production in the lab
  - $Zn(s)+2HCl(aq)= H_2(g)+ZnCl_2(aq)$, i.e. dripping a strong acid over a metal.
  - $Na(s)+H_2O(l)= (1/2)H_2(g)+NaOH(aq)$.
  - $Si(s)+2H_2O(l)=SiO_2(s)+2H_2(g)+339$ kJ/mol. In practice there is an intermediate steps (if not, it is far too slow): $Si(s)+2NaOH(aq)+H_2O(l)=Na_2SiO_3(aq)+2H_2(g)+424$ kJ/mol at room temperature, and $Na_2SiO_3(aq)+H_2O(l)=2NaOH(aq)+SiO_2(s)-85$ kJ/mol at 220 ºC. This technique may become commercial (Si is non-toxic non-CO_2 and non-CO producing, compared to methanol). Presently Si is produced by SiO_2-reduction with charcoal in an electric-arc furnace, producing 10^9 kg/year at 1 €/kg (consuming 29 MJ/kg_{Si} plus 2.7 kg_{coal}/kg_{Si}). Direct electrolysis of molten SiO_2 is not developed. Si is not good for direct fuel (in a SOFC) due to the very small anode voltage. Order of magnitude world production and cost for metals is: Fe 0.2 €/kg, Al $25\cdot10^9$ kg/year at 0.4 €/kg. Pb $40\cdot10^6$ kg/year at 0.4 €/kg, Pt 15000 €/kg.

Reforming a fuel is producing another fuel from it. Several reforming processes exist:

- Partial oxidation (PO), sometimes catalytic (PCO). It is the exothermic reaction with deficient oxygen; it is the simplest reforming process, but gives rise to very high temperatures (2000 K) and pollutants (NO_x, NH_3, HCN) without appropriate catalysts. For methanol reforming, $CH_3OH(vap)+½O_2=2H_2+CO_2+667$ kJ/mol (in reality yields 40% $H_2(g)$ instead of 67%), a Pd catalyst is used. For natural-gas reforming, $CH_4(g)+½O_2=2H_2+CO+36$ kJ/mol (in reality yielding 1.3 mol_{H2}/mol_{CH4} instead of 2), a Pt or Ni catalysts on alumina are used, working at 1200 K (a big problem is the formation of soot, $2CO=C+CO_2$, that clogs the catalyst).

- Steam reforming (SR). It is the endothermic reaction with water vapour; it is the most widely used reforming process and the one that yields more hydrogen, but a very complex one because of the required external heating (only used for production >500 kg/day). Methanol reforming, $CH_3OH(vap)+H_2O(vap)=3H_2+CO_2-49$ kJ/mol (in reality yields 70% $H_2(g)$ instead of 75%, and consumes up to 20% of HHV, at 250 ºC, with Ni plus a final pass through Pt to further oxidise CO to CO_2, $CO+H_2O=CO_2+H_2+41$ kJ/mol; or with Cu/ZnO); although it works for PEFC, it is best suited to PAFC because of the CO_2, and PAFC have the advantage that the vapour is produced with the by-product heat. Natural-gas reforming, $CH_4(g)+H_2O=3H_2+CO-206$ kJ/mol is carried out at 900 K to 1200 K in a gas furnace, with Ni-catalyst on alumina plus a final pass through Pt to further oxidise CO to CO_2; although low pressure favours the reaction, it is not used in practice.
- Autothermic reforming (AR). It is just a combined PO+SR process that it is adiabatic overall; this is presently the most economic method of H_2 production.
- Thermal decomposition (TD). It is the endothermic cracking at high temperature. For methanol, $CH_3OH(vap)=2H_2+CO-95$ kJ/mol (it is not used alone but adding water, i.e. SR). For methane, $CH_4(g)=2H_2(g)+C(s)-75$ kJ/mol, using a Ni-catalyst on silica, that must be regenerated with oxygen from time to time to get rid of the carbon deposited; notice that no CO is involved.
- Carbon-dioxide reforming (not much used). For methane, $CH_4(g)+CO_2(g)=2H_2+2CO-248$ kJ/mol.
- Membrane reactor. It is not reforming itself but a post-processing stage to reforming; after SR (or PO or AR) the gas flow is exposed to a selective membrane that yields 90% H_2.

Storage & transport

History of hydrogen storage and transport is always associated to the Hindenburg-1937 and Challenger-1986 catastrophes (as nuclear energy to the Hiroshima bomb).

Several hydrogen storage systems may be used:

- Compressed gas at 30 MPa and T_{amb} (e.g. 3 kg for 500 km in a car, 0.18 m^3 and 25 kg tank). Requires container inspection every few years. It is the most used storage method for small applications.
- Cryogenic liquid at 20 K and p_{amb} (up to 0.3 MPa really; e.g. 3 kg, 0.10 m^3 and 45 kg tank). With present dewar-tanks it evaporates in two weeks, and it presently costs 35 MJ/kg just to liquefy $H_2(g)$ from ambient conditions (30% of its lower heating value).
- Chemically absorbed in metal hydrides (up to 2%; e.g. 3 kg, 0.05 m^3 of $LaNi_5H_6$), stored by moderate overpressure and/or cooling, and given-off by depression and/or heating. Hydrogen, as most other gases, hardly dissolves in liquids (e.g. 1.6 ppm by weight in water at normal conditions).
- Chemically combined with alkaline metals. A non-flammable non-volatile alkaline aqueous solution of sodium borohydride ($NaBH_4$) at 20%wt, gives off pure $H_2(g)$ by contact with a catalyst (ruthenium, cobalt) at room temperature, by exothermic hydrolysis: $NaBH_4(aq)+2H_2O=4H_2+NaBO_2(aq)$. Power is controlled by insertion/removal of the catalyst.
- Chemically stabilised in clathrates (i.e. metastable crystal networks of host polar molecules like water). Hydrogen clathrates are more difficult to get than methane clathrates; they are realised by slow compression of water and $H_2(g)$ at room temperature up to 200 MPa followed by cooling to

some 250 K. Although this requires a refrigerated storage at 250 K, this could be easily managed for instance with a small venting of innocuous liquid nitrogen vapours.

- Gas trapped in glass micro-spheres or nano-fibres. Very high pressure is needed to put the gas inside, but afterwards the pressure can be lowered without leakage (safe to transport and store), and released by heating.

It is curious that 'hydrogen is roughly as light in air as in water': 7% (of course meaning that the gas has 7% of the density of air, and the liquid has 7% of the density of water, although the last couple can never be in thermal equilibrium).

Safety

Hydrogen is a dangerous flammable gas, with the same self-ignition temperature as methane (850 K), but much wider flammability limits (in air, 4..75% instead of 5..15%), smaller energy for ignition (15 times less), smaller quenching distance (0.6 mm instead of 2 mm), nearly invisible non-premixed flame, and more prone to detonation (in air, detonability limits are 18..59% instead of 6..14%). But, in relative terms to other fuels, hydrogen is not so much dangerous (some claim it is safer), its main advantage being its extreme lightness, which, in ventilated spaces, makes H_2 leaks and flames to vertically escape quickly, minimising possible horizontal spreads (most ignition sources and valuables accumulate horizontally). Hydrogen is not toxic itself, and burns with not toxic fumes (most deaths caused by fire are actually due to deadly fumes and gases).

As further reassurance on H_2 safety, it must be acknowledged that, before natural gas took over, town gas (50% hydrogen) was pipelined to most dwellings in most large cities for nearly a century, with the same or even less damage to people and goods. The often-used stereotypical example of the Hindenburg catastrophe was not due to its lifting hydrogen filling, but to its badly-designed canvass coating, made of a flammable combination of dark iron-oxide and reflective aluminium paints to avoid solar heating. It is concluded now (at the time it was attributed to a H_2-leakage) that, while mooring to a 50 m high metallic docking tower in stormy weather, an electrostatic spark ignited the coating and set fire to everything combustible: the canvas, hydrogen inside the bags, and engine diesel fuel (35 out of the 97 passengers lost their lives, only 8 people by burning, all of them by diesel flames in the cabin; the other victims fall or jumped to the void in despair; a helium-filled air-ship would have had the same type accident and caused the same casualties, it is said).

Hydrogen is most dangerous in poorly-ventilated and closed spaces, due to risk of explosion by deflagration or even detonation. Compressed hydrogen storage poses the additional problem of pressure-vessel explosions, entirely similar to any other compressed gas vessel, but great advances have been recently made on safe-breakage of very high pressure containers made of laminated fibre-reinforced polymers.

Purity

Required hydrogen purity depends on intended use (it is easy to understand that requirements for the ammonia industry are different than those for food hydrogenation). For fuel cell applications, standard purity (e.g. the one offered at the few hydrogen-supply-stations) is compiled in Table 4. A safety problem related to purity is that presently hydrogen cannot be marked with any suitable odorant to ease early leak-detection by humans, as done with all other odourless flammable gases.

Table 4. Admissible impurities in hydrogen supply for fuel cell vehicles.

Component	Tolerance
Inert gases (He+Ar+N_2,…)	<1%
Agua líquida ($H_2O(l)$)	<0.5%
Oxygen (O_2)	<500 ppm
Carbon oxides (CO+CO_2)	<2 ppm
Hydrocarbons (total, including lubricants)	<1 ppm
Sulfur	<1 ppm
Ammonia	<0.01 ppm
Inorganics	<0.01%

Price comparison of hydrogen energy

- Price of an electricity generator, by kW-installed. As for year 2000, electrical utility stations cost 500 €/kW (20-yr life), internal combustion engines 30 €/kW (20-yr life), fuel cells 3500 €/kW (<10-yr life), solar cells 5000 €/kW (<10-yr life).
- Price of energy, by MJ-produced (before taxes). As for year 2000, gasoline 0.006 €/MJ, methanol 0.012 €/MJ, hydrogen 0.020 €/MJ, electricity 0.025 €/MJ (notice that fuel energy refers to its higher heating value).
- As for year 2000, hydrogen costs four times the price of natural gas for the same energy content.

Hint: Hydrogen balloon combustion & explosion

A balloon filled with hydrogen gas burns when ignited but does not produce a large bang. However, if a balloon filled with hydrogen is allowed to remain untouched for a while, oxygen gas from the air begins to effuse through the tiny pores in the balloon material. After a while, the balloon contains a mixture of H_2, O_2 and some other non-reactive gases. When ignited with a lighted candle, the gases inside the balloon quickly react to produce yellow flames and a large bang.

COAL

Coal is the most plentiful fuel available on Earth; proven commercial reserve in 2000 were $>1000\cdot10^{12}$ kg (some 30% in USA, 20% in Russia, 15% in China, 15% in EU-15), but it is a finite, non-renewable and very-polluting source. Estimations in 2000 gave a reserve/consumption ratio of some 250 years.

Coal was known since ancient times, but only used when available on site; most often, a charcoal, a similar stuff obtained from wood, was used (charcoal leaves less ashes, but yields less heat also).

Origin

Coal is a compact black or dark-brown sedimentary rock (a mixture, not a mineral) formed some 300 million years ago (Carboniferous Period, although smaller deposits exists from 200 Myr, dinosaurs era, and 100 Myr ago), by high pressure and temperature anaerobic decomposition of dead plants (mainly ferns), but the degree of metamorphosis varies a lot and several types of coal can be found today;: from more to less ‘cooking’: anthracite, bituminous coal, lignite, and peat.

Types

Coals are classified in a maturity rank according to age and fixed carbon content:

- Anthracite is the hardest, purest, more brittle and scarce coal; too precious for a fuel (it is used for chemicals). It is a dense black solid, with brilliant lustre and very low moisture. (<5% of trapped water).
- Bituminous coal is a dense black solid that frequently contains bright bands with a brilliant lustre. It has some 2..10% of trapped water. Volatile matter range is 10..30%, and the typical heating value is 30 MJ/kg.
- Lignite, or brown coal, is the most abundant form of coal. It has some 40..60% of trapped water. Sometimes, the remaining texture of the original vegetation can be discerned. Volatiles may reach up to 30% in some lignite, and the typical heating value is 15 MJ/kg.
- Peat has some 70..90% of trapped water, and it is not used as commercial fuel (it must be dried to at least 30% in water to be burned, and was used in open fires). Plant decomposition has progressed only partially, and it is possible sometimes to identify the remains of individual leaves in peat, cellulose being still the main component.

Uses

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 (Newcastle coast was plentiful of so-called sea-coal), but mining really took off in the 18th c., also in England, driven by the Industrial Revolution hunger to feed steam boilers. It was after a wood-shortage in West Europe in late 16th c. that coal started to be used in the metallurgical industry, with the coke discovery in 1603 by H. Platt, by heating coal. In the mid 19th c. coal also replaced charcoal in making black-powder and explosives. A great amount of coal is used to make iron (reducing iron ore). Coke, used in blast furnaces to yield clean concentrated heat, is almost pure carbon but amorphous, not as graphite) obtained by anaerobic heating of coal, to separate volatile matter, that is distilled aside.

Coal is not so valued as to worth it deep underground mining; even today, more than half of the world coal is from surface mining (open cut or strip mining), although mines some 500 m deep have been worked (following a surface coal layer deeper and deeper).

Coal had the leading share in world energy production from 1800 to 1950, when oil took over, and still has a large share: 24% of primary energy consumption, mainly restricted to electricity generation in large combustion power plants (38% of world electricity generation).

Since coal consumption in its raw solid form is cumbersome, several fluidification processes have been developed:

- Pulverisation by mechanical grinding.
- Gasification by pyrolysis. Heating coal with air (and preferably also water vapour) produces coal gas (town gas) and leaves a solid residue (coke). In 1792, Murdock, a Scottish engineer, lit his home with gas lamps that burned coal gas. Early in the XIX c, gas lamps had come into use as street lamps in London. The Fischer–Tropsch process (1920s) convert a mixture of carbon

monoxide and hydrogen into liquid hydrocarbons (as done by Germany in II World War; synthetic gasoline was transparent).

- Distillation by pyrolysis. Heating coal in absence of air at >1000 K, produces a mixture of volatiles (CH_4, H_2, CO_2, HCN), a liquid pours out (coal tar), and a solid remains (coke: nearly pure carbon, used in blast furnaces). Coal tar is further distilled: a first fraction yields benzene and toluene, a second fraction naphthalene's, a third fraction creosotes, a fourth anthracenes, and the residue is called coal-tar pitch.

Composition: proximate analysis and ultimate analysis

Coal is a natural composite material, not a single chemical compound, and its composition, being a solid substance, is measured by weight, and referred to either to as-received coal (wet coal), or on a dry basis, or on a moisture-free-ash-free basis. Two types of coal analysis are commonly used:

- Proximate analysis, specifying: fixed coal + volatile coal + ash + water.
- Ultimate analysis, specifying: water + percentage of C, H, O, N, and S.

In any case, coal is first drained, and moisture contents is computed by differential weighting after heating the sample to 103 ºC for several hours. Sulfur content is computed either by chemically converting all S-ions to sulfate-ions and precipitation to $BaSO_4$, or by chemically fixing the sulfur oxides formed on combustion of the sample. Ash is measured as the solid residue on combustion; although there is a difference in composition and weight between initial mineral matter and final ash, the latter is most often used in analysis.

In the proximate analysis, once water is eliminated, volatile coal is computed by differential weighting after heating the dry sample to 950 ºC for several minutes (volatiles consist mainly of H_2, CO, CH_4, C_2H_6, O_2, H_2O and maybe other volatile organic compounds). Fixed coal is computed by subtracting from sample weight moisture, ash, sulfur and volatile coal.

In ultimate analysis, once water is eliminated and sulfur and ash measured aside, the percentage in carbon is measured from CO_2 content of complete burning the sample, the amount of hydrogen is computed as 1/9 of the weight of water produced in combustion, the amount of nitrogen (usually less than 1% in weight) is measured aside or neglected, and the amount of oxygen is computed by subtracting from the total.

A typical dry coal composition is 85% C, 5% H, 5% O and 5% ash by weight). The main impurity in coal combustion has been sulfur: 2..10% in weight. Some sulfur can be removed by just grinding and washing, because it is associated to iron in pyrite chunks that settle, but all modern power plants have flue gas desulfuration units (scrubbers) to get rid of it by absorption in a lime spray.

In summary, coal composition, as received, is as follows:

- 5..15% of moisture, i.e. water mass divided by dry mass (what is left at 103 ºC). Lignites can have 30..60% moisture. Wood moisture is 20..80%.
- 10..20% of ash, i.e. the solid residue after burning. Wood ash is 1..3%.

- The remaining 70..90% is dry ash-free coal, further divided in volatile matter (20..40% by weight in dry ash-free basis) and fixed coal (the solid residue). Overall dry ash-free coal has a composition of:
  - Carbon content in dry ash-free coal is in the range 80..90% by weight. Notice, however, than coal from the mine has less %C by weight (some 70%) than oil (85%) or natural gas (75%).
  - Hydrogen content in dry ash-free coal is in the range 5..6% by weight.
  - Oxygen content in dry ash-free coal is in the range 1..10% by weight (it may range from 1% in dry ash-free anthracite to some 45% in wood just cut). This oxygen decreases both the theoretical air required for complete combustion of the fuel and its heating value, since it is chemically combined with hydrogen and carbon atoms (the HHV reduction per kilogramme of oxygen would be 17.9 MJ/kg if combined with H, or 12.3 MJ/kg if combined with C; a empirical value of 15 MJ/kg is often used, what gives for the higher heating value, HHV=0.33·%C+1.43·%H–0.15·%O in MJ/kg, for the mass-percentages composition).
  - Sulfur is typically 1..5% in dry ash-free coal.
  - Nitrogen is typically 0..2% in dry ash-free coal.

Air requirement for theoretical combustion

Pure carbon demands 11.5 kg of air per kg of fuel, corresponding to 1 mol of oxygen per mol of carbon ($C+O_2=CO_2$) and 23.2% by weight of oxygen in the air. In terms of the dry ultimate analysis of a coal, u%C+v%H+w%O+x%N+y%S+z%Ash, the air demand is the sum of the C-, H-, and S- air-demand, minus the contribution of its oxygen content:

$$A_0=\frac{2.67(\%\mathrm{C})+8(\%\mathrm{H})-1(\%\mathrm{O})+1(\%\mathrm{S})}{23.2}\quad \text{(e.g. } A_0\text{=11.5 kg/kg for \%C=100)}\qquad (1)$$

with typical coal values of A_0=10 kg of air per kg of coal.

Heating values

Pure carbon has a higher heating value of HHV=32.8 MJ/kg, corresponding to the enthalpy of reaction $C+O_2=CO_2+393.5$ kJ/mol. Actual coals would have a heating value made up of the contribution of C-, H-, and S- oxidation, assumed to be bond-free, minus the contribution of the existing bonds, particularly those with oxygen, which could not be further oxidised; i.e. oxygen decreases the heating value for complete combustion, since it is already bonded to hydrogen and carbon atoms.

The HHV reduction per kilogramme of oxygen would be 17.9 MJ/kg if combined with H (286 kJ per half-a-mole of oxygen, $H_2+(1/2)O_2=H_2O+286$ kJ/mol), or 12.3 MJ/kg if combined with C (393.5 kJ/mol per mole of oxygen, $C+O_2=CO_2+393.5$ kJ/mol); an empirical value of 15 MJ/kg is often used, what gives for the higher heating value of a coal in terms of its dry ultimate analysis, u%C+v%H+w%O+x%N+y%S+z%Ash:

$$\frac{\mathrm{HHV}}{[\mathrm{MJ/kg}]}=0.328(\%\mathrm{C})+1.43(\%\mathrm{H})-0.15(\%\mathrm{O})+0.09(\%\mathrm{S})\qquad (2)$$

with typical values in the range HHV=20..30 MJ/kg for soft coal (bituminous coal), HHV=10..20 MJ/kg for brown coal (lignite), and HHV=8..13 MJ/kg for peat and schist (but peat briquettes may reach 17 MJ/kg).

Equations (1-2) can be used for any kind of complex fuel of unknown molecular formula (for which the ultimate analysis per weight is available), either solid (coal, wood), or liquid (gasoline, diesel, heavy fuel or crude-oil).

Price of coal for thermal power plants in 2013 is around 60 $/t (at 30 MJ/kg it means 2 $/GJ, much lower than any other fossil fuel, e.g. natural gas may be 5 times more expensive).

WOOD

Wood is the hard, porous, fibrous substance found beneath the bark of trees and shrubs. Wood is used for timber (construction), for paper making, and as a fuel (up to 30% of wood production in industrialised countries, mostly the debris, but up to 90% in developing countries). Hard wood (resistant to sawing) comes from deciduous broad-leafed trees: oak, elm and fruit trees. Soft woods come from pine, cedar, fir. Paper is made from chemically and mechanically processed wood fibres (typically 30 mm in diameter and 2 mm long) which are self-binding when dried from a wet state.

Composition

Wood is a natural composite material consisting of hollow polymer fibres in a polymer matrix. The hollow fibres are tubular cells (most of them dead), with cellulosic walls (70% cellulose and 30% lignin) holding aqueous solutions in the inside space (water content varies a lot, from 60%wt in freshly cut trees, to 5%wt in artificially-dried furniture-wood); the matrix is made of hemicellulose and lignin. Trees are cut in winter to minimise initial water content.

Chemically, dry wood is an aggregate of 40..45%% cellulose (a long homopolysaccharide, $(C_6H_{10}O_5)_n$ with n=5000..10000 and M=500..10000 kg/mol), 20..30% hemicellulose (a short-chain polymer with n=150..250 and M=20..30 kg/mol) and 20..30% lignin (a reticular polymer with a 3-D structure that glues all together), with some 7% ash (the main components being SiO_2 and CaO); the elementary chemical composition of wood is presented in Table 5. Cellulose, Fig. 2) is the most abundant naturally occurring organic substance; it does not dissolve water, but it forms very porous structure that makes it very hygroscopic (e.g. wood, paper, or cotton, that is practically pure cellulose; pure cellulose is a white crystalline powder).

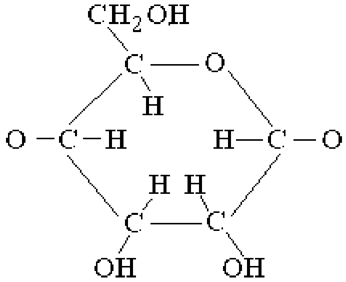

Fig. 2. Molecular structure of cellulose ($(C_6H_{10}O_5)_n$ with n=5000..10000).

Table 5. Wood composition (%wt) and lower heating values.

%wt water→	0	20	40	60
C	50.30	40.24	30.18	20
H	6.20	4.96	3.72	2.7
O	43.08	34.46	25.85	17
N	0.04	0.03	0.02	0.01
S	0.00	0.00	0.00	0.00
ash	0.37	0.31	0.23	0.15
Total	100	100	100	100
LHV kJ/kg	19900	15400	10950	6500

The biological structure of wood is basically a hard hollowed tissue in a cylindrical arrangement. The inner part is mainly xylem (mostly dead conduits of $d_{\mathrm{xylem}}=25\cdot10^{-6}$ m, say between 10 μm and 100 μm; the outermost are alive and allow for water and nutrients supply to the leaves from the roots), whereas the outer part is mainly cambium and phloem (living conduits that return elaborated sap from the leaves to everywhere). Cambium divides every spring, yielding xylem to the interior and phloem to the outside (cambium divides only transversally, increasing the diameter some 2 mm (conifers) up to 7 mm soft woods); apical tissue divides axially, increasing the length). Old xylem vessels (the core or duramen) die and become clogged with dry metabolic wastes, such as tannins, dyes, and resins, just providing structural support to the plant. There is also a tissue that transports water transversally from xylem to cambium (wood rays)

Density. It depends on water and air content (porosity). Maximum is $\rho_{\mathrm{cellulose}}=1550$ kg/m^3, but very soft wood (balsa wood) only has 50 kg/m^3.

Thermal conductivity. It depends on water and air content (porosity), and on direction (anisotropy). Dry wood is a very good insulator due to the air spaces, with $k=0.3$ W/(m·K) along the fibres and $k=0.1$ W/(m·K) transversally.

Heating value. It depends on water content (moisture). Maximum is HHV=20 MJ/kg for dry wood; wood pellets may have HHV=17..18 MJ/kg, log wood HHV=15..16 MJ/kg, and wood chips HHV=13..15 MJ/kg.

Why using wood as a fuel, if a gas or oil burner works smoothly and effortless?. First, there is the case of developing countries where wood is the only fuel, aside of domestic waste. Second, there is the case of wood residues from forest cleaning or industry, which may be used as a commercial fuel instead of just burning it to get rid of. But, besides any practical justification, there is the aesthetic reason of the intrinsic beauty of wood fire and its cultural heritage (our ancestors developed around the fireplace heart). It takes time, effort and thought to burn firewood, but it is creative, inspiring and really warm, bringing you closer to Nature.

Biomass

Here, biomass is synonymous of vegetable matter used as fuel (biofuel), either grown for that purpose, or recovered from other industries waste (forestry, farming, food industry…); urban and animal waste might be included too, but its importance is marginal. Municipal solid waste (MSW) has great organic content and can be used as a fuel in incineration power plants, with HHV=7..12 MJ/kg, but dioxin emission is a problem. It excludes organic material which has been transformed by geological processes into coal, petroleum, or natural gas (fossil fuels).

Biomass is a renewable fuel, and, to a first approximation, carbon neutral, in the sense that the CO_2 released in biofuel combustion was previously captured from the environment during biomass growth, although in October 2007, Nobel Laureate Paul Crutzen published findings that the release of Nitrous Oxide (N_2O) from rapeseed oil, and corn (maize), contribute more to global warming than the fossil fuels they replace.

The traditional biomass through the ages has been wood. Besides the biofuel production here discussed, biomass is also used as a fertiliser (compost), paper industry and other chemical stuff, building (e.g. straw in adobe and roofs, timber), etc.

Biomass can be directly burned in furnaces and boilers, but the preferred way to easy handling and transportation, and to minimise pollution, is by transforming raw biomass into gas (known as biogas or syngas), liquid (which may range from alcohols to tars), and solid (char, pellets…). At present, liquid biofuels (bioethanol and biodiesel) are mixed with oil derivatives (gasoline and diesel) in a 5%..20% biofuel fraction. Table 6 presents some examples of biomass composition:

Table 6. Examples of biomass composition (%wt).

	Sugar cane bagasse	Pine sawdust	Almond shells	Grape stalks
moisture	7	9	12	8
C	46	45	41	41
H	5	5	5	6
O	40	39	39	40
N	0	0	1	0
S	0	0	0	0
ash	1	1	3	5
PCI kJ/kg	16 200	16 400	16 000	16 700

A problem facing energetic crops is the impact on food crop price (the food vs. fuel debate), since, at present, some crops and some fields are of double use, as when cereals are grown for either food or bioethanol, depending on market price, instead of producing the ethanol from cellulose in the straw. An additional problem is the impact on water resources. Presently, most common energy crops are: corn, soybeans, rapeseed, sugar cane, barley, sorghum, palm oil… In the future, biofuels from non-food crops and from algae, should be used.

FUEL PYROLYSIS

Pyrolysis is the chemical decomposition of compounds caused by high temperatures with no access to air or oxygen (i.e. it is not a partial oxidation or combustion process). Most of the times, the decomposition products are separated by distillation (the whole process is called dry or destructive distillation). Pyrolysis implies chemical reactions; the first stages in heating a fuel, up to 400 K, usually imply just a moisture loss (although de-polymerisation may occur after some time). When water is added during the pyrolysis of a fuel, the process is best known as reforming. Recently, catalytic pyrolysis is being developed to drive the process to the most demanding yields. We focus here on pyrolysis of some raw fuels (wood, coal, crude oil, biomass) to get more suitable fuels. Pyrolysis is the major step for crude-oil cracking in the petroleum industry to get lighter fuels (and to get ethylene and hydrogen for synthetic chemicals).

The earliest use of pyrolysis was to produce coke (a smokeless form of coal without volatiles, with more than 80%wt carbon, used in metallurgy and as a fuel), by heating coal to more than 1200 K. The vapours can be cooled to get a liquid condensate (known as coal tar) and then distilled to yield, as a first batch up to 500 K, a mixture of benzene, toluene and xylene; from 500 K to 550 K mainly naphthalene, from 550 K to 600 K mainly creosotes, and from 600 K to 650 K a mixture of quinoline, anthracene and phenanthrine, leaving a solid residue called coal-tar pitch, used as a heavy fuel or as a binder in making coal or coke briquettes. Similar organic products are obtained from the pyrolysis of any natural organic material: wood, coal or crude oil.

Wood and wood residues are basically cellulose, like paper. When heated, up to 100 ºC (<400 K), wood tends to dry, i.e. to loose moisture by evaporation, and some internal depolymerisation starts, slowly decreasing wood strength. Between 100 ºC to 200 ºC (400..500 K), non-combustible products are released, as water vapour, carbon dioxide and other trapped gases. Above 200 ºC (>500 K) the cellulosic polymers decompose yielding volatile organic compounds, with a weight loss of some 10% from 100 ºC to 300 ºC (400 K to 600 K). Above 400 ºC (>700 K) all volatile material is gone, with a sudden 80% weight loss from 300 ºC to 400 ºC (600 K to 700 K), and a carbonaceous char (charcoal) remains (charcoal is often approximated as pure carbon, but it is really partially pyrolysed cellulose best approximated by the empirical formula C_7H_4O). In the presence of air, the flash point is around 250 ºC (500 K), giving a slow-burning glow or a prominent flame according to the heat losses, and the autoignition is around 400 ºC (700 K). A now-obsolete method for making methyl alcohol (wood alcohol) was to pyrolyse wood chips and separate the volatile alcohol by fractional distillation.

Pyrolysis of biomass (straw and other agricultural feedstock, or organic wastes from the cellulose, paper and sugar industries) generates three different energy products in different quantities: coke (char), oils (tar) and gases (syngas). In low-pressure fast pyrolysis the biomass is fast heated and allowed to decompose into vaporised oils that are fast cooled and condensed, in order to eliminate any polymerisation. In catalytic high-pressure pyrolysis the biomass is heated at a high pressure with a reducing gas and a catalyst, and a synthetic gasoline is produced.

Pyrolysis of plastics and rubbers, taking place in most uncontrolled fires, produce very toxic gases. Some plastics decompose to their monomers (e.g. (PE, PMMA), whereas others generate new substances, as when PVC decomposes to HCl). High-temperature resisting plastics decompose to almost-exclusive carbonaceous residue.

Table 7. Thermal softening, decomposition, and heating value of some materials.

Material	Density ρ [kg/m^3]	Softening T_g	Decomposition T_d	Minimum ignition T_{flas}	Autoignition $T_{self\text{-}ign}$	Combustion HHV [MJ/kg]

Bakelite (Phenol-formaldehyde, PF)	1300	NA	250 ºC	-	-	-
Cellulose (90% in cotton)	1600	NA	280 ºC	300 ºC	400 ºC	17
Coal	1400	NA	200 ºC	-	-	28
Methacrylate (PMMA)	1180	85 ºC	180 ºC	300 ºC	450 ºC	26
Nylon (Polyamide, PA)	1140	220 ºC	300 ºC	450 ºC	500 ºC	32
Polyacrylonitrile (PAN)		-	250 ºC	450 ºC	550 ºC	-
Polyester	1380	260 ºC	-	-	-	18
Polyethylene (PE)	930	100 ºC	350 ºC	350 ºC	370 ºC	46.5
Polypropylene (PP)	910	170 ºC	350 ºC	350 ºC	370 ºC	46
Polystyrene (PS)	1040	100 ºC	300 ºC	350 ºC	500 ºC	42
Polyurethane (PU)	1100	NA	-	300 ºC	400 ºC	-
PVC (polyvinylchloride)	1400	75 ºC	200 ºC	350 ºC	450 ºC	20
Teflon (PTFE)	2250	330 ºC	500 ºC	550 ºC	600 ºC	-
Wood	~500	NA	200 ºC	300 ºC	400 ºC	25

NA. Not Applicable (e.g. glass-transition temperature is not applicable to thermosetting polymers)

Cellulose is the most abundant polymer on earth. Like most polymers it is not a well-defined molecule but a family of closely related chemical structures known as polysaccharides, consisting of long unbranched chains of H-bond-linked glucose units, $-(C6H10O5)_n-$ with n=300..2000, with size of order 10^{-7} m and M~50..300 kg/mol. The linear chain is very coiled, masking the H-bonds and making cellulose highly insoluble in water, but it forms very porous structure that make it very hygroscopic (e.g. paper). Cellulose is the main constituent of plant cell walls, but not digestible by humans; if its hydrolysis, saccharification and fermentation were mastered (like in ruminants and some insects like termites), it would be a less expensive source of glucose than starch.

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