<u>The stoichiometry of burning hydrocarbon fuels</u>

The power produced by an internal combustion engine is determined solely by the quantity of fuel it can burn during a given interval of time, just so long as the engine holds together. An engine with a large swept volume can produce a given amount of power while turning at a lower RPM than a smaller engine, but both engines will produce the same amount of power if they burn the same amount of fuel.

The fuel may be gasoline, diesel, ethanol or some combination of them. When the fuel is combined with oxygen, the reaction which converts the molecules of fuel into byproducts like carbon dioxide and water releases heat. The reaction is said to be "exothermic", "exo" meaning "giving out to its surroundings" and "thermic" describing the heat so given out. The heat produced by the reaction causes the gas in the combustion chamber to expand, pressing down on the piston head.

All of these fuels – gasoline, diesel and ethanol – consist primarily of hydrocarbons, a general name for molecules whose constituent atoms are hydrogen and carbon. There are always some impurities, such as sulphur, but most of the fuel consists of hydrocarbon molecules of "various lengths". Why various lengths?

The nucleus of any atom is a combination of protons and neutrons. The number of protons in the nucleus determines the type of atom it is. If it has 6 protons, it is a carbon atom. If it has one proton, it is a hydrogen atom. If it has 8 protons, it is an oxygen atom. If it has 92 protons, it is a uranium atom. The number of neutrons which float around in the nucleus of an atom is not exactly fixed. For example, a carbon atom can have 6, 7 or 8 neutrons, but it will always have exactly 6 protons, which is what makes it a carbon atom. The type of carbon with 6 neutrons happens to be much more common than the type with 7 neutrons; about 99% of the carbon on Earth is C^{6+6}. The type of carbon with 8 neutrons is actually unstable. After a period of time, it will explode. One of the neutrons will fire off an electron, converting itself into a proton. The nucleus changes from 6 protons and 8 neutrons to 7 protons and 7 neutrons. Since the number of protons has changed, it is no longer a carbon atom. It is a nitrogen atom. We call the act of firing off of an electron a "decay" event, and the fact that C^{6+8} decays in this way means that we call it "radioactive".

Everything described in the previous paragraph relates to the <u>nucleus</u> of an atom. In an internal combustion engine, we are interested not in the nucleus, but in the shells of electrons which orbit around the nucleus. When a reaction affects the electrons in an atom, it is called a "chemical" reaction; when a reaction affects the nucleus, it is a nuclear reaction.

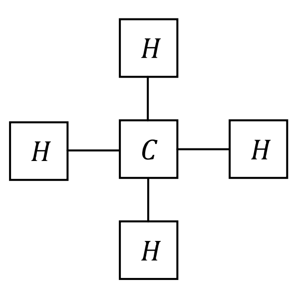
An atom in its normal state is electrically neutral, and the number of electrons orbiting the nucleus will be equal to the number of protons in the nucleus. An electron has one negative unit of electrical charge and a proton has one positive unit of electrical charge. In a carbon atom, the six positive units of electrical charge contained in the nucleus are exactly balanced by the negative charge on its six electrons. However, it is not too hard to knock one of the electrons out of a carbon atom. Electrical circuits powered by five to 100 volts, including batteries, are enough to knock an electron or two out of most atoms. When an electron is removed from an atom, the atom is no longer electrically neutral. Removing one electron from a carbon atom leaves it with one net positive unit of electrical charge. We use the names "ions" to describe atoms which are not electrically neutral. Ions do not have to be positive; they can also be negative. In fact, some atoms have a tendency to add one or more electrons, so they are often encountered as negative ions. Batteries, as an example, are devices which hold a group of positive ions in one region and a group of negative ions in a separate region. When the two groups are allowed to mix, which they will do when one of the regions is connected by wire to the other, the two groups will react in such a way that causes electrons to flow in one direction down the wire.

Let me return to the carbon atom and its six electrons. Electrons orbiting a nucleus have a tendency to arrange themselves in layers, not unlike the layers of an onion. Unlike the layers of an onion, which vary with the size of the onion, the layers of electrons around atoms have certain very fixed sizes. The innermost layer (of any atom) can hold a maximum of two electrons. The second layer (of any atom) can hold a maximum of eight electrons. The third layer also holds eight. And so on, with a specific maximum number of electrons in each layer. Any particular layer of electrons is most stable when it contains exactly the maximum number of electrons for that layer. What kind of atom has exactly two electrons to fill the innermost layer? Well, an atom with two electrons will be electrically neutral if it has two protons. The nucleus of a helium atom has exactly two protons. Helium is therefore very stable from a chemical point-of-view. What kind of atom has exactly ten electrons, two to fill the innermost layer and eight to fill the second layer? A nucleus with ten atoms is a neon atom, which is also very stable from a chemical point-of-view. In fact, the atoms with completely-filled layers of electrons are those elements which form the right-most column in the periodic table. From the top, they are Helium (2 protons and 2 electrons), Neon (10 protons and 10 electrons), Argon (18 protons and 18 neutrons), Krypton (36 protons and 36 neutrons), Xenon (54 protons and 54 neutrons) and Radon (86 protons and 86 neutrons). All of these are very stable from a chemical point-of-view. There are no stable atoms which are bigger than these. This is not because the layered electrical shells become unstable, but because the nuclei of bigger atoms themselves are unstable and blow apart.

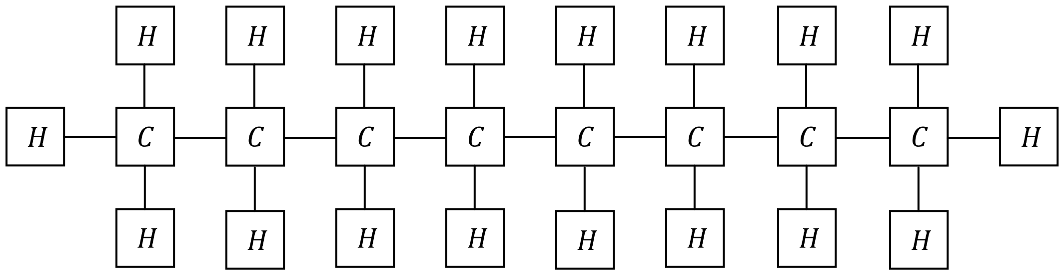
Atoms which do not have completely-filled shells of electrons are unhappy. They tend to look for atomic partners who can help them fill the unused places in their outer-most shells. This is possible because two atoms which are placed in close proximity can actually share an electron. For example, an atom which has exactly one electron in its outer-most shell is a natural partner for an atom which is one electron short in its outer shell. A good example which we eat every day is salt. Its sodium atom (11 protons and 11 electrons) has two filled layers (with 2 and 8 electrons, respectively) but only one "loose" electron in its third layer. Salt's chlorine atom (17 protons and 17 electrons) has two filled layers (with 2 and 8 electrons, respectively) but the 7 electrons in its third layer are one short of completion. A shared-electron makes both the sodium and chlorine atoms happy. The reason is energy. It takes less energy for an atom to exist (live?) with a complete electron shell than it does to exist with only a partial shell. While a shared electron is not quite as good (meaning lowest energy) for an atom as having its very own electron would be, it is much better than having an incomplete shell.

Carbon and hydrogen are also a natural pair of atoms. A hydrogen atom (1 proton and 1 electron) has only one electron, and is therefore one electron short of a complete 2-electron inner layer. A carbon atom (6 protons and 6 electrons) has four electrons in its second layer, four less than the magic eight. The 4:1 ratio means that carbon and hydrogen don't team up in pairs, like sodium and chlorine do. But they do team up. The way they do it is this.

Four hydrogen atoms snuggle up against one carbon atom. The electron of each hydrogen atom is shared with a missing place in the carbon shell. This combination of atoms, which we write as CH_4, is a molecule of methane. Conceptually, a molecule of methane looks like this.



Another common way for carbon and hydrogen to team up is in a chain like the following.



The electron of each hydrogen atom is shared with one and only one carbon atom. Note that a carbon atom can share one of the electrons it does have in its outer shell with a neigbouring carbon atom. The two carbon atoms at the end of the chain each team up with three hydrogen atoms and one carbon atom. The carbon atoms in the middle of the chain each team up with two hydrogen atoms and two carbon atoms.

This kind of chain can obviously come in various lengths. We have different names for the different lengths. The following table matches the name to the total number of carbon atoms, and gives the chemical symbol for that kind of molecule.

Name of fuel	**Number C atoms on ends**	**Number C atoms in middle**	**Total number of C atoms**	**Chemical symbol**
Methane	1	0	1	CH_4
Ethane	2	0	2	C_2H_6
Propane	2	1	3	C_3H_8
Butane	2	2	4	C_4H_{10}
Pentane	2	3	5	C_5H_{12}
Hexane	2	4	6	C_6H_{14}
Heptane	2	5	7	C_7H_{16}
Octane	2	6	8	C_8H_{18}
Nonane	2	7	9	C_9H_{20}
Decane	2	8	10	$C_{10}H_{22}$

The molecular layout in the drawing at the top of this page has six carbon atoms in the middle, plus two on the ends, for a total of right carbon atoms. It is an octane molecule. The prefix in the names – "hex", "hept", "oct" and so on – are the Latin roots for the total numbers of carbon atoms in the molecule. The number of hydrogen atoms is always equal to twice the number of carbon atoms, plus two.

Methane and ethane are gases under normal atmospheric conditions and can only be liquefied at very high pressures. Moderate pressures are sufficient to liquefy propane, so it can be conveniently stored as a liquid in steel bottles. Butane is so easily liquefied that it is widely used in cigarette lighters and other applications where a small amount of fuel is needed. It is the heavier molecules, hexane through decane, which are the principal components of the common automotive fuels.

The simplest hydrocarbon molecule, methane, burns according to the following reaction:

$$CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2 + \text{ energy}$$

One molecule of methane and two molecules of oxygen (with each molecule of oxygen consisting of two atoms of oxygen), come together, re-arrange their components, and then move apart. The three molecules which exist after this encounter are two molecules of water vapour (H_2O)and one molecule of carbon dioxide (CO_2). Energy is produced during the encounter.

When there is a macroscopic mixture (meaning that it is big enough to see) of methane gas and oxygen gas, containing millions of millions of molecules, the above reaction will occur millions of millions of times. A couple of questions arise. Will all of the methane and oxygen be used up, or "burned"? And, are there other ways in which methane and oxygen can combine with each other?

In order for all of the methane and all of the oxygen to be used up, they have to be present in the original mixture in exactly the right proportion. There have to be exactly twice as many oxygen molecules as there are methane molecules. Whether we measure the quantities by weight or by volume, we have to make sure that the number of molecules present has the ratio two-to-one. This ratio is called the "stoichiometric ratio" for this particular reaction. It is a statement of the molecule-to-molecule ratio required for this reaction. A perfect reaction which consumes all of the oxygen and all of the methane is hard to achieve. Not only does the number of molecules have to be right, but they have to be well mixed and sufficient time must be given for everything to happen according to plan.

To answer the second question: yes, there are other ways in which methane and oxygen can react. If there is not enough oxygen, the methane can still react, and will do so in a way which uses less oxygen per methane molecule. Two methane molecules can react with three oxygen molecules in the following way:

$$2\ CH_4 + 3\ O_2 \rightarrow 4\ H_2O + CO$$

The byproducts from this reaction are water (as before) and carbon monoxide. But, no energy. Or, to be more precise, much less energy than given off by the previous reaction. This reaction is not an optimal way to burn methane, assuming by "optimal" that one wants to maximize the energy produced.

The optimal combustion reactions for methane, ethane, propane, butane and pentane, which have one, two, three, four and five carbon atoms, respectively, are as follows:

Methane:	$CH_4 + 2\ O_2$	$\rightarrow 2\ H_2O + CO_2 +$ energy
Ethane:	$C_2H_6 + 3½\ O_2$	$\rightarrow 3\ H_2O + 2\ CO_2 +$ energy
Propane:	$C_3H_8 + 5\ O_2$	$\rightarrow 4\ H_2O + 3\ CO_2 +$ energy
Butane:	$C_4H_{10} + 6½\ O_2$	$\rightarrow 5\ H_2O + 4\ CO_2 +$ energy
Pentane:	$C_5H_{12} + 8\ O_2$	$\rightarrow 6\ H_2O + 5\ CO_2 +$ energy

There is a clear pattern here. In general, the optimal combustion reaction for a hydrocarbon molecule with n carbon atoms is the following:

$$C_nH_{2n+2} + \frac{3n+1}{2}\ O_2 \rightarrow (n+1)\ H_2O + n\ CO_2 + \text{ energy}$$

It is important to see that all of these hydrocarbon fuels burn the same ratios of reactant (input) atoms. For each n carbon atoms, there are $2n + 2$ hydrogen atoms and $3n + 1$ oxygen atoms. Note that these are atoms, not molecules.

C atoms	H atoms	O atoms
n	$2n+2$	$3n+1$

In order to avoid fiddling around with pressures and densities when the reactants are gases, it is convenient to measure the reactant gases by mass. Let's work through an example, starting with the atomic weights of the three types of reactant atoms: carbon, hydrogen and oxygen.

The absolute mass of one carbon atom is $1.660538921 \times 10^{-27}$ kilograms. The huge number of significant digits is given because carbon happens to be used by scientists as the basis for measurements of "AMU". One AMU, or atomic mass unit, is exactly one-twelfth of the mass of one atom of carbon in its rest state. The AMU is not an S.I. unit, but is frequently used anyway. Single atoms of carbon, hydrogen and oxygen weigh 12 AMU, 1 AMU and 16 AMU, respectively.

The following table sets out the masses involved in the burning one octane molecule.

Reactant	**Mass of one atom**	**Atoms in one reaction**	**Mass in one reaction**
Carbon	12 AMU	$n = 8$	$12 \times 8 = 96$ AMU
Hydrogen	1 AMU	$2n + 2 = 18$	$1 \times 18 = 18$ AMU
Oxygen	16 AMU	$3n + 1 = 25$	$16 \times 25 = 400$ AMU

Let's scale this up. Instead of burning just one molecule of octane, let's burn, say, 10^{26} molecules. We will multiply the last column in the previous table by 10^{26} and then convert the AMU's into kilograms.

Reactant	**Mass in 10^{26} reactions**	**Mass in 10^{26} reactions**
Carbon	96×10^{26} AMU	15.941 kg
Hydrogen	18×10^{26} AMU	2.989 kg
Oxygen	400×10^{26} AMU	66.422 kg
Total		85.352 kg

Of course, carbon and hydrogen atoms don't come in separate packages. They are combined in the fuel. The weight of the fuel is the sum of the carbon weight and the hydrogen weight, $15.941 + 2.989 = 18.930$ kg.

Nor does the oxygen come separately, at least not in normal automotive applications. Normal automobiles take their oxygen from the atmosphere. Assume that we are powering the engine with air at "standard" conditions. There are many technical variants of "standard" conditions, but most are based on dry air (no humidity) at sea level, at room temperature on a day with average atmospheric pressure. Oxygen gas (O_2) makes up only 23.20% of dry air <u>by weight</u>. The more common statement, that the ratios of oxygen, nitrogen and other gasses in the atmosphere are 21% : 78% : 1%, is based on a comparison <u>by volume</u>. 286.302 kilograms of dry air therefore contain $23.20\% \times 286.302 = 66.422$ kilograms of oxygen, the desired amount.

The masses of fuel and air needed for 10^{26} reactions are:

18.930 kilograms of octane fuel and 286.302 kilograms of dry air

The ratio of air-to-fuel is 286.302 / 18.930 = 15.124. This is the stoichiometric ratio by which pure octane fuel is burned in dry air at standard conditions. This ratio is more commonly called the Air-Fuel Ratio ("AFR"). It varies slightly depending on the type of fuel. This variation in the ratio is <u>not</u> caused because different amounts of oxygen are needed. That is definitely not the case – the number of oxygen molecules needed for each fuel molecule is always the same. What does vary is the relative weight of carbon and hydrogen in the fuel molecules themselves. An octane molecule has eight carbon atoms and 18 hydrogen atoms, so 8/26 = 30.8% of the atoms are carbon. A hexane molecule has six carbon atoms and 14 hydrogen atom, so 6/14 = 42.9% of the atoms are carbon. This difference propagates through the calculations and results in different

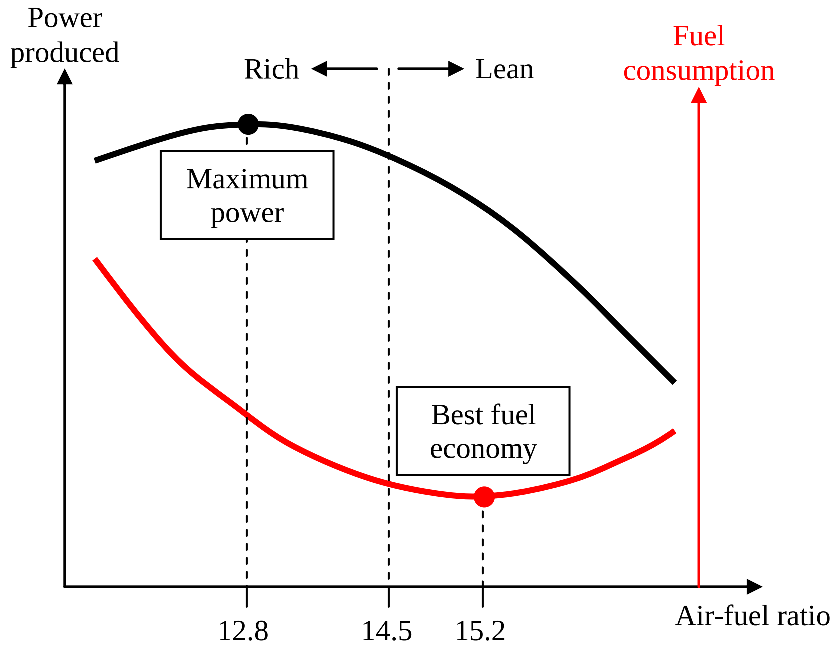
AFRs. In the following table, we have repeated in summary form the calculations we did for octane fuel. The table assumes 10^{26} molecules of each fuel are burned.

Fuel	**Ratio of atoms C : H : O in one reaction**	**Masses in AMU C : H : O for one reaction**	**Masses in kg C : H : O for 10^{26} reactions**	**Masses in kg fuel : air**	**AFR**
Hexane	6 : 14 : 19	72 : 14 : 304	11.956 : 2.325 : 50.480	14.281 : 217.588	15.237
Heptane	7 : 16 : 22	84 : 16 : 352	13.949 : 2.657 : 58.451	16.605 : 251.944	15.172
Octane	8 : 18 : 25	96 : 18 : 400	15.941 : 2.989 : 66.422	18.930 : 286.302	15.124
Nonane	9 : 20 : 28	108 : 20 : 448	17.934 : 3.321 : 74.392	21.255 : 320.656	15.086
Decane	10 : 22 : 31	120 : 22 : 496	19.926 : 3.653 : 82.363	23.580 : 355.012	15.056

The table shows fuels with up to ten carbon atoms. The AFR ratio decreases as the fuels get heavier. But, the hydrocarbon chains do not stop with just ten carbon atoms. There are longer chains, and their AFR ratios get progressively lower.

The heavier fuels have molecules which weigh more than the molecules of the lighter fuels. When petroleum is distilled, or refined, it is heated inside a vertical tube. Under the force of gravity, the heavier molecules gravitate towards the bottom of the tube, displacing the lighter molecules which float towards the top. Various taps along the side of the vertical tube enable the oil company to extract fluids from various heights along the tube. Liquids taken from higher up along the column contain a greater percentage of lighter molecules than liquids taken for lower taps. Gasoline is drawn off from somewhere near the middle. Diesel is drawn off from a tap further down. Diesel is therefore a heavier, lower grade, fuel than gasoline. (The stuff near the bottom is Bunker C.) It therefore happens that diesel has a lower Air-Fuel Ratio than gasoline. A good measure of the quality of a fuel is what percentage of octane, one of the lightest of the molecular chains, it contains.

A common rule of thumb is that the AFR for gasoline is 14.7 and that for diesel is 14.5. These are a little less than the stoichiometric AFR for octane, for several reasons. As just discussed, both gasoline and diesel contain some heavier hydrocarbons. Secondly, most engines are tuned to run slightly rich. There are reasons why an engine should be run with an air-fuel ratio slightly different from the stoichiometric ideal. An engine can be run "lean" with more air than the AFR or it can be run "rich" with less air than the AFR. The following curve shows a couple of performance characteristics which illustrate the tradeoff.



Running an engine at exactly its stoichiometric AFR makes it run very hot. Surprisingly, one of the most important results of running either lean or rich is that it reduces the temperature. In both settings, the mixture which passes through the cylinders includes unreacted gas – extra fuel in a rich mixture and extra air in a lean mixture – both of which carry away some of the heat.

There are other factors, too, which can cause the desired AFR to depart from the stoichiometric ideal. Impurities in the fuel, like sulphur, reduce the percentage of the fuel mass which actually consists of combustible hydrocarbons. Less oxygen / air is needed to burn a given mass of this fuel than a purer fuel. That has the effect of lowering the operating AFR Humidity in the ambient air has the opposite effect. "Humidity" is a measure of the amount of water vapour in the air. Water vapour is simply free molecules of H_2O which have not condensed into a liquid. They add to the mass of a given volume of air, but do not contribute to combustion. More humid air is needed than dry air for a given amount of fuel, hence a higher AFR. Air density, which is affected by both the ambient pressure and temperature, do not affect the AFR. Air may have different density on different days, but the difference in density does not by itself change the composition of the air. It will be necessary to deliver a greater or lesser volume of air to the engine to make available the same mass of oxygen, but the AFR will not be changed. Modern engine control systems have sensors that can detect and compensate for many factors like these.

One of the biggest challenges facing engine designers is the mechanism of bringing the fuel and oxygen into contact. The fuel in the tank is in a liquid state – it must be vapourized into a gas before combustion will occur. Then, the fuel gas must be well mixed with the oxygen. The desired reactions can only occur if the two gases are in very close proximity at a molecular level. Finally, sufficient time must be provided for the reactions to be completed. An engine running in its red zone at 5,000 RPM has a crankshaft which makes one revolution in one-five thousandth of a minute, or 0.012 seconds. There is a power stroke in each cylinder once every second revolution. The compression stroke, during which the gases are introduced into the cylinder and mixed together, can last no longer than one-half of a revolution, or 0.006 seconds, or six milliseconds. Engines made before the 1960s often suffered from incomplete mixing and combustion. That could be compensated for by adding extra air. Engineers made a lot of progress during the 1970s and 1980s understanding the processes by which the gases mix and burn in the cylinders, and designed cylinders, pistons and reactant delivery systems to suit. The combustion which takes place in a modern well-tuned engine is very close to the ideal.

Jim Hawley

If you found this description helpful, please let me know. If you spot any errors or omissions, please send an e-mail. Thank you.