# FUEL COMBUSTION

Where does the energy that drives the motors come from? What are hydrocarbons made of? Why does it need air to burn fuel? What is the amount of energy released by combustion? How to calculate the efficiency of an engine? What do the exhaust gases contain? What releases are considered pollutants and how are they eliminated? These are the questions we answer here.

## Oil and hydrocarbons

Fuels for engines of cars, boats or planes are called hydrocarbons, a term that refers to any molecule made up of hydrogen and carbon atoms.

The hydrocarbons are obtained by refining crude oil extracted from the subsoil.

How did oil form? Like natural gas and coal, it was formed from the slow decomposition of vast forests that covered the globe during the Primary age, forests that were buried in the subsoil or submerged during the Carboniferous period, about 300 million years ago. So, the expression of fossil energy is used to designate this kind of energy.

## Fuels

Fuels differ according to their components.

The analysis of samples of pure and non-additive fuels shows that the diesel fuel consists (by mass) of 87% of carbon (symbol C) and 13% of hydrogen (symbol H); the gasoline consists of 84% carbon and 16% hydrogen; the LPG, a mixture of liquid butane ($C_4H_{10}$) and propane ($C_3H_8$), consists of 82% carbon and 18% hydrogen.

These proportions make it possible to establish the fictitious chemical formulas of each of these fuels, which will be used later to calculate all the other parameters of the combustion. Thus the diesel fuel formula is $C_{7.25}H_{13}$; the gasoline formula is $C_7H_{16}$; the LPG formula is $C_{3.5}H_9$.

## Earth's atmosphere

The analysis of the Earth's atmosphere shows that, except for local pollution, the ambient air consists (by mass) of 76% nitrogen gas (chemical symbol $N_2$), 23% oxygen gas (chemical symbol $O_2$) and 1% rare gases (in descending order: argon, neon, helium, krypton and xenon) and various molecules (carbon dioxide, steam).

These proportions make it possible to establish the chemical formula of the ambient air: $O_2 + 3.8\ N_2$. In this calculation, rare gases (which are chemically neutral) and other minor components have been assimilated to nitrogen gas.

## The combustion

Observe a piece of dead wood left in the open air for a while: nothing special happens.

Crack a match and put it in contact with the piece of wood: it ignites almost instantly, it is combustion.

How to explain this phenomenon? The heat of the match communicated both to the piece of wood and the surrounding atmosphere, has caused a connection between the main component of wood, carbon(1) and one of the components of the air, oxygen (nitrogen is present but does not intervene in combustion). The result, besides a release of heat, is the formation of carbon dioxide ($CO_2$ chemical symbol).

What role did temperature play in this reaction? The temperature reflects the amount of agitation of the atoms within the molecules(2). As the temperature rises, the agitation increases, weakening the existing chemical bonds to favor new ones.

Indeed, the affinities between atoms are more or less strong. For example, oxygen shows no attraction for the nitrogen with which it coexists in the air(3), while it has strong affinities for many other elements, especially for carbon and hydrogen.

This phenomenon is the starting point of the fuel combustion: if the temperature is high enough, the carbon (C) and the hydrogen (H), weakly bound together within the hydrocarbon molecule, capture oxygen from the air ($O_2$) to form carbon dioxide ($CO_2$) and water ($H_2O$). This reaction releases a large amount of energy, mainly in the form of heat, this is its interest.

## The Lavoisier principle

The famous principle of Antoine de Lavoisier (French chemist, 1743-1794) states that "*nothing is lost, nothing is created, everything is transformed*". In other words, a chemical reaction is a transformation without mass variation.

By virtue of this principle, a chemical equation must always be perfectly balanced, that means that the number of atoms must always be strictly identical before a reaction and after, whether these atoms have changed partners or not. Hence the notion of stoichiometry.

## La combustion des hydrocarbures

Stoichiometry (from the Greek "*stoikheion*", element, and "*metron*", measure) refers to the study of ideal proportions of elements that allow a complete and clean chemical reaction. This law applied to the combustion of hydrocarbons shows us that:

- the combustion of 1 kilogram of diesel fuel requires about 14.6 kilograms of air (that is, given the composition of the air, about 11.2 kilograms of nitrogen and 3.4 kilograms of oxygen); the reaction produces about 11.2 kilograms of nitrogen (this gas being chemically neutral, it did not participate in the combustion), 3.2 kilograms of carbon dioxide ($CO_2$) and 1.2 kilograms of water ($H_2O$).

- the combustion of 1 kilogram of gasoline requires about 15.3 kilograms of air (that is, given the composition of the air, about 11.8 kilograms of nitrogen and 3.5 kilograms of oxygen); the reaction produces about 11.8 kilograms of nitrogen (this gas being chemically neutral, it did not participate in the combustion), 3.1 kilograms of carbon dioxide ($CO_2$) and 1.4 kilograms of water ($H_2O$).

- the combustion of 1 kilogram of LPG requires about 15.6 kilograms of air (that is, given the composition of the air, about 12 kilograms of nitrogen and 3.6 kilograms of oxygen); the reaction produces about 12 kilograms of nitrogen (this gas being chemically neutral, it did not participate in the combustion), 3 kilograms of carbon dioxide ($CO_2$) and 1.6 kilograms of water ($H_2O$).

## The energy released by combustion

Various laboratory experiments have accurately measured the exact amount of energy released by the burning of simple bodies.

So, burning one kilogram of carbon releases an energy of about 33 million joules; burning one kilogram of hydrogen releases an energy of about 120 million joules.

Knowing the mass composition of a hydrocarbon, it is then easy to deduce the total energy that it can release during its combustion in an engine:

- the combustion of one kilogram of diesel fuel of formula $C_{7.25}H_{13}$ releases a net energy of about 41.7 million joules; taking into account the density of the product (845 $kg.m^{-3}$), that means about 35.2 million joules per liter;

- the combustion of one kilogram of gasoline of formula $C_7H_{16}$ releases a net energy of about 43.7 million joules; taking into account the density of the product (760 $kg.m^{-3}$), that means about 33.2 million joules per liter.

- the combustion of one kilogram of LPG of formula $C_{3.5}H_9$ releases a net energy of about 45.1 million joules; taking into account the density of the product (550 $kg.m^{-3}$), that means about 24.8 millions of joules per liter.

Note: the net energy (also called LCV, 'lower calorific value') is obtained after deduction of the energy corresponding to the vaporization of water (change of state, that is to say transition from the liquid state to the gaseous state), about 2.26 $MJ.kg^{-1}$.

## The efficiency of an engine

What happens to the energy released by combustion? It appears in two distinct forms: heat and movement.

The heat is the same as one can feel in front of any fire. The heating of a car engine is a normal phenomenon. Alas, this heat is useless, aside from heating the cabin, so it is doomed to dissipate in the environment.

Movement is what you need to keep the car going. In the case of an automobile engine, the pressure of the gases in the combustion chamber causes the movement of the pistons and the rotation of the crankshaft, tangible sign that another part of the released energy has manifested itself in the form of movement(4).

How to distinguish these two forms of energy? Simply by calculating the efficiency of the engine. In fact, this calculation is defined as the ratio between the energy recovered and the energy consumed.

In the case of a car engine, the energy recovered is measured at the end of the crankshaft on a power bench (expressed in kilowattheure(5), symbol kWh); the energy consumed corresponds to the mass of fuel burned (expressed first in kilograms, then converted into joules). The result is dimensionless.

Example: let's calculate the efficiency of a diesel engine that has consumed 1 kg of diesel fuel to produce an energy of 5 kWh.

$$(5 \times 3\,600\,000) / (1 \times 41\,700\,000) = 0.43$$

This result means that 43% of the energy consumed in the form of diesel fuel appeared as movement, here the rotation of the crankshaft. Therefore the remaining 57% appeared as heat transferred to the environment(6).

## Combustion in real conditions

Perfect stoichiometry is always difficult to guarantee, even in the laboratory, especially because of the contamination of the air or of the components used in the experiments, but it can be approached.

It's very different when it comes to burning fuel inside an automotive engine that runs in real-world conditions.

Indeed, not only the fuel may have differences in composition depending on the country and the distributors, but in addition, the air mass introduced into the engine varies continuously depending on the ambient temperature and atmospheric pressure.

It should be added that car engines never operate at constant and ideal rotation speeds, or temperatures or workloads, that means that the amount of fuel injected into the cylinders must be changed in real time.

**Pollutant releases**

When the laws of stoichiometry are observed, the exhaust gas contains only nitrogen gas ($N_2$), carbon dioxide ($CO_2$) and steam ($H_2O$). These bodies exist in large quantities in nature, they are chemically stable and are essential in order to maintain natural balances, they are not pollutants. But what happens when the laws of stoichiometry are no longer respected?

Consider two opposite configurations: rich mixture (too much fuel, not enough air) and lean mixture (little fuel, too much air).

In the first configuration, some atoms of the hydrocarbon molecule do not find an "oxygen partner" in sufficient numbers because the air is missing, so they are not completely oxidized and end up in the exhaust gases as carbonaceous particles, or unburned hydrocarbons (chemical symbol HC) or carbon monoxide (chemical symbol CO), a gas that should not be confused with $CO_2$: one is very toxic, the other not at all (see ADILCA file ‘‘*carbon dioxide*’’).

In the second configuration, excess of air (this is the case when the engine is supercharged) strongly compressed at high temperature (this is particularly the case of diesel engines) can form nitric oxide (symbol NO), because of the chemical reaction between oxygen ($O_2$) and nitrogen ($N_2$). Once expelled, nitric oxide has the particularity to spontaneously transform into nitrogen dioxide (chemical symbol $NO_2$) when exposed to air, generating a mutation of atmospheric oxygen to ozone (chemical symbol $O_3$). Both of these gases are very toxic to living organisms (see ADILCA file ''*nitrogen dioxide*'').

**Anti-pollution systems**

How did the manufacturers manage to solve the combustion problems in real conditions?

Increasingly stringent anti-pollution standards have forced manufacturers to radically change engine power systems. The antediluvian carburetors with inaccurate dosages were replaced by electronic injection coupled with an intake sensor (to account for the intake air mass) and a 'lambda' probe at the exhaust, all supplemented by an oxidation catalyst. The quantity of fuel injected is thus optimized, while the "lambda" probe continuously measures the conductivity of the exhaust gases ("lambda" value), in other words their carbon monoxide content. In case of imbalance, this probe drives the injection with instant correction of the richness of the mixture. For its part, the catalyst is responsible for oxidizing the possible pollutants by associating them with the missing oxygen atoms. The emissions of unburned hydrocarbons and carbon monoxide are thus perfectly controlled.

Anti-pollution standards evolve permanently (EURO V, EURO VI ...). The new challenge is the emission of nitrogen oxides, a counterpart to the exceptional performance of engines. The currently most effective technique is to inject an ammonia solution (chemical symbol $NH_3$) into the exhaust line in order to obtain a reduction (in the chemical sense of the term) of the nitrogen oxides ($NO$-$NO_2$) and transform them into nitrogen gas ($N_2$) and steam ($H_2O$).

(1) *The wood cellulose (chemical formula $C_6H_{10}O_5$) contains 44.4% carbon, 49.4% oxygen and 6.2% hydrogen (by mass). If you slowly heat a piece of wood inside an oven, the more volatile components burn up first, leaving the piece of wood gradually turning into a black-colored glowing mass that reveals a high concentration of carbon.*

(2) *This agitation corresponds to the speed of the molecules, which can reach very high values (400 $m.s^{-1}$ for the air molecules at normal temperature and pressure) and that explains the pressure exerted on the internal surface of the container; in case of a liquid or a solid, this agitation corresponds to the vibrations of the different atoms which compose the matter.*

(3) *More or less stable bonds can be established between atoms under conditions of very high pressure and temperature, this is the case between oxygen and nitrogen inside the engine, a reaction that produces nitric oxide (NO chemical symbol). Nitric oxide is spontaneously transformed into nitrogen dioxide (chemical symbol $NO_2$) when exposed to air.*

(4) *These two forms of energy (heat and movement) are self-balancing: if the resistance of the pistons becomes too strong, the temperature and pressure in the combustion chamber rise immediately, thereby increasing the force exerted on the pistons, etc.*

(5) *The kilowattheure (symbol kWh) is an energy unit: 1 kilowattheure = 3,600,000 joules.*

(6) *In this example, the 43% of energy appearing as movement will also end up as heat with the heating of the transmission, wheel bearings, tires, molecules of air disturbed by the passage of the car, brakes (or bodywork in the event of a collision). Ultimately, all the raw energy released by the combustion of fuel appears, sooner or later, as heat. Movement is therefore only a temporary form of thermal energy.*

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# SOME CHEMICAL REACTIONS

**Atoms molar mass (kg.kmol$^{-1}$):**

hydrogen (**H**): 1
carbon (**C**): 12
nitrogen (**N**): 14
oxygen (**O**): 16

**Molecules density (kg.m$^{-3}$ at 273 K and 1,013 hPa):**

nitrogen ($N_2$): 1.25
oxygen ($O_2$): 1.43
carbon dioxide ($CO_2$): 1.96
water ($H_2O$): 1,000
diesel fuel: 845
gasoline: 760
LPG: 550

**Chemical formula of pure air** (*rare gases considered as nitrogen*)**:**

mass: oxygen ($O_2$) 23 %; nitrogen ($N_2$) 77 %

- molar mass of oxygen: 16 x 2 = 32 kg
- molar mass of one kilomole of oxygen: (32 / 23) x 100 = 139 kg
- mass of nitrogen: 139 – 32 = 107 kg
- molar mass of nitrogen: 14 x 2 = 28 kg
- nitrogen index: 107 / 28 = **3.8**

chemical formula: $O_2 + 3.8\ N_2$

**Diesel fuel formula:**

mass: carbon (**C**) 87 %; hydrogen (**H**) 13 %

carbon index: 87 / 12 = **7.25**; hydrogen index: 13 / 1 = **13**

chemical formula: $C_{7.25}H_{13}$

**Gasoline formula:**

mass: carbon (**C**) 84 %; hydrogen (**H**) 16 %

carbon index: 84 / 12 = **7**; hydrogen index: 16 / 1 = **16**

chemical formula: $C_7H_{16}$

## LPG chemical formula:

LPG mass: butane ($C_4H_{10}$) 50 %; propane ($C_3H_8$) 50 %

chemical formula: $C_{3.5}H_9$

## Diesel fuel combustion:

$$C_{7.25}H_{13} + 10.5\ O_2 + (10.5 \times 3.8)\ N_2 \rightarrow 7.25\ CO_2 + 6.5\ H_2O + 40\ N_2$$

$C_{7.25}H_{13}$: diesel fuel
$O_2$: oxygen
$N_2$: nitrogen
$CO_2$: carbon dioxide
$H_2O$: water

Considering the molar mass of each element of this reaction, one obtains the following proportions:

1 kg of diesel fuel + 3.36 kg of oxygen + 11.2 kg of nitrogen
→
3.19 kg of $CO_2$ + 1.17 kg of water + 11.2 kg of nitrogen

Considering the density of each body involved in this reaction, one obtains the following proportions:

1 liter of diesel fuel + 1,985 liters of oxygen + 7,570 liters of nitrogen
→
1,375 liters of $CO_2$ + 1 liter of water + 7,570 liters of nitrogen

## Gasoline combustion:

$$C_7H_{16} + 11\ O_2 + (11 \times 3.8)\ N_2 \rightarrow 7\ CO_2 + 8\ H_2O + 42\ N_2$$

$C_7H_{16}$: gasoline
$O_2$: oxygen
$N_2$: nitrogen
$CO_2$: carbone dioxide
$H_2O$: water

Considering the molar mass of each element of this reaction, one obtains the following proportions:

1 kg of gasoline + 3.52 kg of oxygen + 11.76 kg of nitrogen
→
3.08 kg of $CO_2$ + 1.44 kg of water + 11.76 kg of nitrogen

Considering the density of each body involved in this reaction, one obtains the following proportions:

1 liter of gasoline + 1,870 liters of oxygen + 7,150 liters of nitrogen
→
1,195 liters of $CO_2$ + 1.1 liter of water + 7,150 liters of nitrogen

**LPG combustion:**

$$C_{3.5}H_9 + 5.75\ O_2 + (5.75 \times 3.8)\ N_2 \rightarrow 3.5\ CO_2 + 4.5\ H_2O + 22\ N_2$$

**$C_{3.5}H_9$**: LPG
**$O_2$**: oxygen
**$N_2$**: nitrogen
**$CO_2$**: carbon dioxyde
**$H_2O$**: water

Considering the molar mass of each element of this reaction, one obtains the following proportions:

1 kg of LPG + 3.6 kg of oxygen + 12 kg of nitrogen
→
3 kg of $CO_2$ + 1.6 kg of water + 12 kg of nitrogen

Considering the density of each body involved in this reaction, one obtains the following proportions:

1 liter of LPG + 1,390 liters of oxygen + 5,320 liters of nitrogen
→
850 liters of $CO_2$ + 0.875 liter of water + 5,320 liters of nitrogen

**Total energy produced by fuel combustion:**

Diesel (density 845 $kg.m^{-3}$): **44.3 $MJ.kg^{-1}$** (**37.4 $MJ.l^{-1}$**)

Gasoline (density 760 $kg.m^{-3}$): **46.9 $MJ.kg^{-1}$** (**35.6 $MJ.l^{-1}$**)

LPG (density 550 $kg.m^{-3}$): **48.7 $MJ.kg^{-1}$** (**26.8 $MJ.l^{-1}$**)

**Net energy produced by fuel combustion:**

Diesel (density 845 $kg.m^{-3}$): **41.7 $MJ.kg^{-1}$** (**35.2 $MJ.l^{-1}$**)

Gasoline (density 760 $kg.m^{-3}$): **43.7 $MJ.kg^{-1}$** (**33.2 $MJ.l^{-1}$**)

LPG (density 550 $kg.m^{-3}$): **45.1 $MJ.kg^{-1}$** (**24.8 $MJ.l^{-1}$**)

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