



# hydrogen **safety**: a **failsafe technology** as key to **social acceptance**

If hydrogen is to become a prevalent energy carrier, its widespread utilization will require technologies of foolproof safety, as regards production, storage, and distribution, a favorable environmental balance sheet, together with rigorous regulation. Public acceptance, which is already being assessed on the ground during experiments, may only be secured on such terms.

Hydrogen nozzle in a service-station run by Shell Hydrogen in Iceland, under the aegis of the ECTOS Program. Identification and control of the risks associated to this fuel must bring it to the same safety level as any other.



## Acceptability of the hydrogen pathway

Gaining acceptance for the notion that hydrogen is no more dangerous than natural gas or gasoline, and that it is merely different is a challenge that education and demonstrations should make it possible to meet.

**F**ear of **hydrogen** is very real, even though the notorious "Hindenburg syndrome," arising from the destruction of the German airship of that name at Lakehurst, New Jersey in 1937, probably unfairly redounded against this pathway. According to a NASA scientist, indeed, the fire that destroyed the airship was set off by an electrostatic discharge around the flammable material making up its outer envelope, rather than explosion of the hydrogen stored in the gas cells, which merely burned. There does remain the fact that the accident would have been less fierce, had the airship been filled with helium...

This controversial instance only goes to show that the challenge to be met should not be obfuscated: acceptance of the hydrogen pathway cannot be taken for

granted, and such a delicate issue should be addressed pragmatically, by making plain to the public, and government, by way of information and demonstrations, that hydrogen is no more hazardous than **natural gas** or gasoline - it is merely different. And that the objective risk associated to it can be controlled, provided that safety is a concern taken in from the design stage, for facilities and systems.

The various aspects relating to acceptability of the pathway are detailed in what follows, be it hydrogen safety (risk assessment, simulation, experimentation), technology standards (**ISO** standards), environmental impacts ("well-to-wheel" evaluation), or the socio-economical impacts on a modern urban society (as instanced by the Icelandic ECTOS Program).

# The hydrogen risk reassessed

The safety issues relating to the flammability and explosive properties of hydrogen gas are well controlled in industry. They must be equally so with regard to use by the public at large.

**H**ydrogen is a serious candidate, as regards becoming the **energy carrier** of tomorrow, to complement electricity. It offers the very major benefit of completely clean combustion, since its **oxidation** yields neither **greenhouse-effect** inducing **carbon dioxide**, nor any other pollutant gas noxious to health. Moreover, used in **fuel cells**, it allows electricity to be obtained with a very high efficiency.

Widespread use of hydrogen does however raise many technical issues, which CEA, along with others, is addressing: production, storage and distribution, and, cutting across these topics, safety issues, relating to the flammability and explosive properties of this gas. Indeed, even if hydrogen is a gas very well known and understood, and use of which has been mastered, in an industrial context, its use by the public at large calls for technologies of foolproof safety, along with rigorous regulation. The expertise grown by CEA, in particular through modeling of the "hydrogen risk" in pressurized-water nuclear power stations, and in the context of French and international programs, should enable a significant contribution to be made to mastery of this risk, and public acceptance of this energy carrier. At the European level, CEA is an active participant in the HySafe network of excellence set up under the aegis of the 6th Framework Program, bringing together twenty-six partners, with the aim of promoting safe utilization of hydrogen.

## A well-defined risk

Hydrogen is not a toxic gas. The risk it presents arises from its flammability and explosivity. It may thus, in this respect, be compared to **natural gas** (consisting essentially in **methane** [CH<sub>4</sub>]), use of which is widespread. Use of hydrogen is not necessarily any more hazardous, however the risk involved is somewhat different. This should be taken on board, therefore, in the design of installations. Comparison with **propane** and gasoline fumes (see Table) is equally instructive. Significant points to bear in mind, in terms of risk, are six:

- hydrogen is 8 times lighter than methane, and its molecule, being very small, confers to hydrogen a very good diffusion coefficient in air (nearly 4 times that for methane). In an unconfined environment, hydrogen thus tends to rise, and dilute very rapidly into the atmosphere, which is a factor making for safety;
- hydrogen is the chemical species carrying most energy per unit mass. On the other hand, per unit volume of gas, theoretical explosive energy is 3.5 times lower for hydrogen than for natural gas;
- the lower flammability limit (the concentration below which a mixture can no longer support combustion) stands at 4% by volume, comparable to that of natural gas (5% by volume). On the other hand, the upper flammability limit (the concentration above which a mixture stops being flammable) is markedly higher (75%, as against 15%), increasing the combustion risk for hydrogen-rich concentrations that may form in the vicinity of a leak;



Mistra facility, at CEA/Saclay, for investigation of the release of hydrogen (experimentally simulated by helium) in a confined environment.

	hydrogen H <sub>2</sub>	propane C <sub>3</sub> H <sub>8</sub>	natural gas (methane CH <sub>4</sub> )	gasoline (fumes)
molecular mass (g/mol)	2	44	16	
density (atmospheric conditions) (kg/m <sup>3</sup> )	0.08	1.87	0.7	
heating value (lower) (kJ/g)	120	46	50	44,5
flammability domain limits in air (vol%)	4.0 – 75.0	2.1 – 9.5	5.3 – 15.0	1.0 – 7.6
minimum ignition energy (mJ, for a stoichiometric mixture at ambient pressure and temperature)	0.02	0.26	0.29	0.24
autoignition temperature (°C)	585	487	540	228 – 501
flame temperature (°C)	2,045		1,875	2,200
detonation limits (vol%)	13 – 65		6.3 – 13.5	1.1 – 3.3
combustion rate in air (in atmospheric conditions) (cm/s) [laminar flame speed]	265 – 325	30 – 40	40	
explosive energy (kg TNT/m <sup>3</sup> )	2.02	20.3	7.03	44.24
diffusion coefficient in air (cm <sup>2</sup> /s)	0.61		0.16	0.05
flame speed in air (cm/s)	260		37	
detonation velocity in air (km/s)	2		1.8	

Table.  
Comparative properties of hydrogen, propane, methane, and gasoline fumes  
(source: HyWeb, INERIS and AFH<sub>2</sub>).



Bus fitted with Ullit natural gas tanks. Demonstration operations are intended, in particular, to show that hydrogen is no more dangerous than natural gas or gasoline.

- the energy required to ignite hydrogen, at **stoichiometric** concentration, is also much lower (some 10 times lower) than for natural gas or propane;
- a hydrogen flame emits little radiation, which, in the event of a fire, limits the risk of propagation due to heat radiation effects. On the other hand, the pale blue flame is scarcely visible in daylight, which may constitute a hazard for emergency and rescue services;
- a hydrogen flame propagates at a much higher velocity (about 7 times faster) than a natural gas flame, and the risk of **detonation** (an explosion, with a very large blast effect) may not be ruled out altogether.

For an assessment of the risk presented by hydrogen combustion or detonation, and of the means to mitigate the consequences, it is crucial that the reaction mechanisms be well understood.

## From ignition to combustion

### Conditions for ignition

The energy required to initiate a **deflagration** (minimum ignition energy) in a hydrogen-air mixture is very low - of the order of 0.02 mJ for a stoichiometric mixture, at ambient pressure and temperature. Spark ignition occurs if the elementary combustion wave set off by the spark has exceeded a critical radius by the time the discharge ends. Ignition of the gas mixture may also occur through contact with a hot body. However, estimation of the temperature such a body must attain is not straightforward, since this depends on gas temperature in the vicinity, gas composition, and heating kinetics. For instance, if gas circulation is taking place in a **turbulent** regime, the temperature of that body must be higher, since exchanges are more effective, and, consequently, temperature falls off more rapidly. Ignition may occur if there is a region in the gas where temperature reaches a value close to that pertaining to a flame propagating in an equivalent mixture. Minimum energy for the direct initiation of detonation is a function of hydrogen content: it stands at 5 kJ for a stoichiometric hydrogen-air mixture. There are thus 5 orders of magnitude separating the amount of energy required to ignite a deflagration, and that for a detonation. Direct initiation of a detonation is commonly deemed to be unlikely, considering the amounts of energy involved. However, a detonation may be initiated from a deflagration, as a result of an

acceleration process caused by turbulence-combustion interaction, or a shockwave focusing process, or emergence of "hot spots." This is referred to as deflagration-to-detonation transition (DDT). These highly complex mechanisms, the physics of which is not as yet fully understood, will require R&D efforts for some ten years yet.

### The flammability domain

The lower flammability limit stands at 4 vol% hydrogen in air. A number of factors influence this flammability limit: the direction of flame propagation, the presence of inerting gases (i.e., gases promoting a reduced occurrence of combustion), pressure, and temperature.

The lower limit for upward vertical propagation is 4 vol% hydrogen in dry air, at normal pressure and temperature. For downward propagation, in the same conditions, the limit stands at 9 vol% hydrogen (the buoyancy effect having to be overcome, since, as a result of the Archimedean force, burned gases tend to rise); finally, for horizontal propagation, the limit is set at 6 vol%. The value to be considered is thus 9 vol%, for propagation in all directions. As a conservative estimate, for the purposes of analysis, the lower limit is taken as being 4 vol% hydrogen in dry air.

The inerting effect may be purely thermal (increased heat capacity of the mixture), or chemical (perturbation of the reaction mechanism). As a rule, the inerting agent acts on all characteristics (autoignition temperature, initiation energy...), since these are linked, reflecting as they do alterations in the thermochemistry or chemical kinetics.

### Subsonic deflagration and supersonic detonation

Deflagration is a combustion mode characterized by flame propagation through **heat conduction** and molecular diffusion, at a speed lower than the speed of sound in the reactive medium. Once initiated, the deflagration propagates as long as gas mixture conditions (composition, temperature) allow the chemical reaction to sustain itself. The propagation speed of such a deflagration is thus the outcome of a combination of specific characteristics of the gas mixture, and of the flow prevailing in unburned gases, downstream from the chemical reaction zone. The fundamental propagation speed is defined as the velocity of the flame front, relative to unburned gases, in laminar flow conditions.

As a result of instabilities, and interaction with the flow (turbulence), propagation speed may then rise. The first threshold value corresponds to the speed of sound in unburned gases, above which there necessarily arises in the gas mixture, ahead of the flame, a shockwave, or a system of shockwaves, of varying intensity, altering the state of the unburned gases, and interacting with the combustion zone. In this acceleration process, turbulence may increase the flame's propagation speed, however it may equally lower it, as a result of too intense turbulence in the mixture. It would appear that, subsequently, the speed of sound in the burned gases forms a more or less stable point, as regards propagation speed ("shocked" flame regime). Finally, the flame can ultimately undergo transition to detonation, as a result of complex mechanisms involving chemical kinetics, turbulence and acoustic processes. To sum



up, a detonation is a combustion mode occurring through autoignition of the mixture, compressed by the associated shockwave, and propagating at supersonic speed, relative to the reactive medium.

As regards sensitivity of the mixture to flame acceleration, specific experiments have allowed an empirical criterion to be arrived at (s criterion, where s stands for the thermal expansion coefficient, i.e. the ratio between the densities of unburned and burned gases, in combustion taking place at constant pressure), providing a necessary condition for flame acceleration. This criterion is associated to an inherent characteristic of the gas mixture (obtained via **thermochemistry**), bearing no relation to the geometry of the environment through which the combustion propagates. However, it does allow a first analysis to be carried out.

Detonation of hydrogen-air mixtures has been the object of a major R&D effort, following the accident, in 1979, at the Three Mile Island nuclear power station, in the United States. Stoichiometric mixtures are the most highly detonable. All detonation limits found in the literature are a function of the diameter of the tube (or of the characteristic length of the experimental setup) in which detonation was set off, and may not be taken as being universally valid for a given mixture, at a given pressure and temperature. Detonations have been observed for mixtures holding 11.7-75 vol% hydrogen at 20 °C, and 9.5-77 vol% hydrogen at 100 °C, in the absence of inerting agents. Detonation cell size (cells presenting a "fish-scale" pattern) may be taken as one of the characteristic parameters for a detonation. To simplify, such cells provide an image of the three-dimensional propagation pattern of a detonation. Cell size should not be considered, in the first analysis, as yielding a sufficient condition, but rather a necessary condition. Curvature of the detonation front, due to effects from the walls, is a further important parameter. The literature provides an analytical formula, for the evaluation of detonation cell size as a function of mixture composition, temperature, and percentage of steam content. A rise in temperature, from 20 °C to 100 °C, reduces this size by a factor of about 2. On the other hand, for every increase by 10% steam content, detonation cell size increases by a factor 3. Experimental uncertainty concerning measurement of this parameter is of the order of a factor 2. The major R&D efforts carried out over the past two decades have enabled a number of empirical criteria (necessary conditions) to be arrived at, relating to the existence, propagation and transmission of detonations. These criteria involve comparison of  $\lambda$ , this being the detonation cell size (sensitivity of the mixture taken on its own), with a characteristic geometrical dimension of the installation where such a detonation is liable to occur, a dimension it is the expert's remit to identify. Such criteria allow an initial analysis to be made, of the hydrogen detonation risk (see [Box](#)).

### Means of prevention

A number of strategies exist, to counter the hydrogen risk, according to the constraints attaching to the installation. Some of these were specifically investigated in the context of control of this risk in nuclear power stations, and their implementation with respect to hydrogen-using systems has yet to be considered. Three such

## Empirical criteria for initial risk assessment

A number of empirical criteria allowing initial assessment of the hydrogen risk to be carried out may be mentioned, by way of example:

- tube size for which a detonation can propagate is of the order of one third detonation cell size;
- transmission of a detonation from a confined environment to a large adjacent space is governed by the following criteria:  $D = 13 \lambda$ , for a tube of diameter  $D$ ;  $A = 3 \lambda$ , for a channel of rectangular section ( $A \times B$ , with  $A < B$ ); and  $D = 11 \lambda$ , for a channel of square section (of side  $D$ );
- one necessary condition for initiation of a detonation from the acceleration of a flame in an installation of characteristic dimension  $D$  is that  $D$  be of the order of  $7 \lambda$ . This criterion does not cover jet ignition situations (stringent geometrical constraints), or conditions of high concentration gradients.

strategies may be cited, by way of example. Inerting, through addition of a gas such as nitrogen, is a solution for small components. Passive catalytic recombination, as recommended in power stations run by French national electricity utility EDF, consists in use of devices that gradually consume hydrogen, to keep concentrations below critical thresholds. Finally, ignition, i.e. igniting a flame in the vicinity of a source, by means of spark, glow-plug or catalytic igniters, results in preventing too heavy accumulation of the gas, thus precluding detonation.

As regards applications involving use of hydrogen, however, ventilation is certainly the best means of diluting the gas into the surrounding atmosphere, thus bringing down the risk of formation of an explosive cloud, as shown by one of the following examples, in a confined environment.

### CEA risk-assessment tools

CEA has been designing for some years computation tools to simulate both hydrogen dispersion and hydrogen combustion. The organization has also devised experimental facilities to investigate accident phenomenology.



Gas-sampling system of the Mistra facility, at CEA/Saclay. Connected to a mass spectrometer, this allows mappings of concentration fields to be drawn up for the simulated hydrogen inside the vessel.

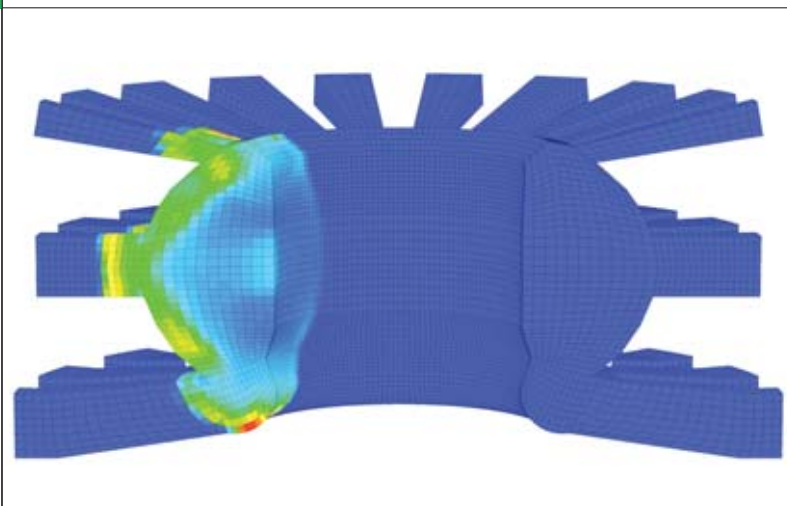


Figure 1.  
Computation of an air-hydrogen detonation in the vacuum vessel of the ITER thermonuclear fusion reactor, carried out with the CAST3M code: pressure field, ranging from 1 to 13 bars, 3 milliseconds after initiation of a detonation in a stoichiometric region (unrealistic scenario).

Most simulation tools were developed for the analysis of nuclear safety issues: for instance, the Tonus application of the CAST3M computation program (code) was developed in collaboration with IRSN, to assess the hydrogen risk associated to loss-of-coolant accidents in pressurized-water reactors. CAST3M was also used in safety investigations concerning the ITER thermonuclear fusion reactor <sup>(1)</sup> (see Figure 1), in an admittedly unrealistic - accident scenario, which in all event served as numerical benchmark for the purposes of a "code-to-code" validation between the simulation code developed by the Karlsruhe, Germany Research Center (FZK), and that from CEA.

Utilization of that same code for safety investigations relating to such applications as the hydrogen vehicle is also ongoing, under the aegis of the HySafe Program. It is thus enabling investigation of the effect of ventilation (presence of vent-holes in confined premises) on hydrogen accumulation, and thus on the explosion risk (see Figure 2). Other tools developed at CEA can

■ (1) In this respect, see Clefs CEA No. 49 (Spring 2004).

equally be applied to simulation of accidental breaching of hydrogen storage systems, in particular for the investigation of accidental **cryogenic** tank depressurization events.

For experimental purposes, CEA can further avail itself of such in-house resources as, for instance, the CESTA (Centre d'études scientifiques et techniques d'Aquitaine: Aquitaine Scientific and Technological Research Center) facilities, near Bordeaux, for the investigation of explosions, or MISTRA, at Saclay, allowing investigation of accidental release of hydrogen (simulated by helium) in a confined environment. This facility indeed allows concentration and velocity measurements, for a variety of flow conditions, ranging from jet to plume regime. CEA's computation tools and experimental resources are due to be called on for added-value services, in the near future, under the aegis of the HySafe network of excellence.

## Suitable standards and regulations

If risks are to be limited, apparatus standardization must be developed, and suitable regulation drawn up. Presently, there is in France no specific regulation addressing use of hydrogen as an energy carrier. Current regulation, highly restrictive as it is, indeed applies to centralized hydrogen production installations in the chemical industry. Specific regulation thus has to be drawn up, or extant regulation must be adapted, for the storage, distribution or use of hydrogen, particularly in installations using fuel cells. For the hydrogen vehicles of the future, drafting of regulations is taking place at the European, and indeed international, level. A European program (EIHP: European Integrated Hydrogen Project), in which CEA is a participant, brings together the major automotive manufacturers, equipment manufacturers, gas suppliers, oil companies, and a number of research centers, to draft the basis for specific regulation for hydrogen. Two proposals for regulations concerning vehicle onboard (liquid, or compressed gaseous) hydrogen tanks are already under discussion in Geneva, in the context of international technical agreements, under the aegis of organizations emanating from the United Nations Organization. It may thus be hoped

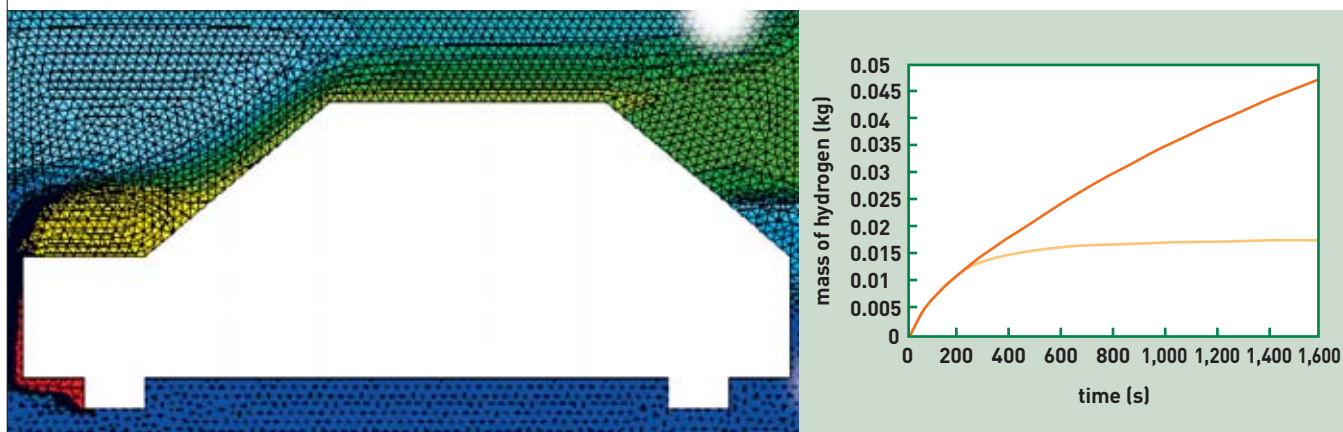


Figure 2.  
Investigation of the effect of ventilation [presence of one or two vent-holes] in a personal vehicle garage, for an accidental hydrogen leak. Left, hydrogen concentration field, this ranging from 4% (red zone), through 2% (green), to close to 0% (blue). Right, curve showing the evolution of the overall mass of hydrogen inside the garage box as a function of time; this shows the beneficial effect of ventilation, with respect to the hydrogen risk (dark curve: one vent-hole; light curve: two vent-holes).

that, within a few years, the outcome will be some international regulation, concerning hydrogen-fueled vehicles.

Standardization also plays a major role with respect to safety. While not having statutory force, it does provide an incitement to use the best manufacturing and control techniques, and facilitates attainment by manufacturers of quality and standardization levels such as to enable regulations to be readily met. Here also, CEA has an active presence, since it is responsible, together with **Afnor** and **UTE**, for the steering of two mirror committees, representing France in international technical committees: ISO TC197 Hydrogen Technologies, and IEC TC105 Fuel Cell Technologies.

Towards a fuel as safe as any other

Use of hydrogen as an automotive vehicle fuel is nowadays a technical reality. For this pathway to develop, it is essential that there be a capability to ensure the risks associated to this fuel are properly identified, and controlled, and make it as safe as any other. The HySafe Program should enable the drawing together, at the European level, of R&D efforts in this domain, and thus promote the rise of a European safety culture.

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The restrictive regulation applying to hydrogen production and storage installations, for hydrogen as a chemical feedstock, will have to be adjusted to cater for storage, distribution and use of hydrogen as an energy carrier.

## Assessment of the environmental impact of hydrogen pathways

The main benefit expected from introduction of hydrogen as a fuel is with respect to environmental concerns. One further reason to ensure the various conceivable pathways are investigated, for the purposes of a rigorous assessment of their global impact in this respect. A "well-to-wheel" assessment, for transportation - or "source-to-service," for other applications - is a requisite, since hydrogen, ultimately, is as "clean" as the energy used to produce it, and transport it.

The drive to counter climate warming is one of the two main motives, along with the end of cheap oil, for the introduction of **renewable energy sources** into the transportation sector, and in particular of **hydrogen** as a vehicle **fuel**. There is now a broad consensus as to the fact we are already experiencing global climate change, caused by emissions of **CO<sub>2</sub>** and other **greenhouse gases (GHGs)**, mainly due to the burning of **fossil** fuels. The consequences include, among other phenomena, increasingly violent storms, and a rise in occurrence of extreme climate events, such as droughts, heavy rainfalls, and consequent floods. However, mainly in industrialized countries, emissions from the transportation sector keep rising. This is true of GHG emissions, as, to a lesser extent, of local pollutants such as **nitrogen oxides (NOx)**. Curbing, and subsequently bringing down, such emissions, in particular from personal vehicles, is thus an urgent requirement.

For the future, use of renewable energy sources for transportation is the only sustainable solution, if climate is to be preserved, and energy supplies secured. In particular, this is the only way that may be envisaged, of meeting mobility requirements for the populations of developing countries.

This is why hydrogen as a vehicle fuel is an option gaining increasing attention from automotive manufacturers, protagonists in the energy sector, and political decision-makers. This was evidenced, in particular, by the setting up, at the behest of the **European Commission**, of the European Hydrogen and **Fuel Cell** Technology Platform. This initiative takes on board the rapid technological advances made over the past few years, with respect to development of novel, clean, high-efficiency motors and powertrains for fuel-cell vehicles. It further expresses the recognition of the many opportunities afforded by hydrogen, as regards a mitigation of environmental issues.





## From ecobalance to "well-to-wheel" assessment

Life-cycle analysis of a product is a standardized method (ISO 14040) for the assessment of that product's environmental impacts throughout its life cycle (consumption of natural resources, atmospheric and waterborne emissions, waste generation), from extraction of natural resources to disposal of waste. This analysis, sometimes also referred to as *ecobalance*, is a detailed quantitative assessment of inputs and outputs, as measured at the boundaries of the system. On the other hand, the costs generated by the product's life cycle may only be evaluated through a complementary method, such as life-cycle costing. In the case of **fuel** - including **hydrocarbon fuel** - pathways, in particular for a hydrogen pathway, the preferred analysis is a "well-to-wheel" (for transportation sector applications) or "source-to-service" (for other applications) assessment, as regards the pathway's energy requirements and atmospheric emissions, which does not formally involve a life-cycle analysis. All processes involved in the energy chain are then taken on board: primary energy supply, and hydrogen production, transport, storage, distribution and use.

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### The most flexible fuel

Of all fuels, hydrogen is the one offering the greatest flexibility in terms of feedstocks, since it may be obtained from both fossil and renewable energy sources (see *How is hydrogen to be produced?*). Hydrogen may be produced in decentralized plants, in service-station forecourts, or in centralized installations, for instance close to large wind-turbine farms, or hydroelectric power stations.

Compressed gaseous hydrogen, produced from **natural gas** and used in fuel-cell vehicles, would result in greenhouse gas emissions lower by 25%, compared to a vehicle directly using natural gas.

If fuels are produced from renewable energy sources, greenhouse gas emissions, along with other ecological impacts (resulting solely from production, and utilization, of so-called gray energy), are kept very low. Such impacts correspond, essentially, to the construction of production plants, and vehicle manufacture. With a rising share of renewable energy sources in the overall energy offer, the share of renewable energy used in construction of energy generating plants, and in vehicle manufacture, will rise in turn. As a result, GHG emissions attributable to production and use of gray energy will come down.

Hydrogen obtained from renewable energies thus appears as the best path, with respect to such emis-

sions. It offers the best option, as a fuel obtained from **biomass**, although various pathways for such production differ greatly as to emissions of GHGs, depending on specific conditions.

This energy carrier has the greatest potential, in the long term, of becoming the sustainable fuel for the transportation sector. It offers benefits in terms of potential GHG reduction, for a whole range of supply pathways. "Well-to-wheel" analyses (see *Box*) are required, however, to sort out the issues: in particular, it is not so much the fuel itself as the combination of fuel and vehicle that must be examined. <sup>(1)</sup>

Finally, use of hydrogen in fuel cells generates no local emissions whatsoever, making any depollution technology at the exhaust superfluous.

### The tool developed by consultants LBST

Recent international "well-to-wheel" studies, seeking to evaluate a variety of advanced fuel and vehicle options, have used the E<sup>2</sup>database tool developed by German consultants **LBST**, acting as a partner, in France, with CEA and **IFP**. This tool models the various processes involved in an energy chain, connecting them by way of relations between inputs and outputs, to calculate the energy requirements and greenhouse gas emissions for the entire chain, from well (primary energy supply) to wheel (end use in a vehicle). A new version of this tool (E<sup>3</sup>database) has just been developed, including, in particular, a cost computation functionality, as part of the scientific and technical partnership between LBST, CEA, and IFP.

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(1) The findings from the exhaustive investigations analyzing all these points (the General Motors Well-to-Wheel Analysis of Energy Use and Greenhouse Gas Emissions of Advanced Fuel/Vehicle Systems - A European Study; and the joint CONCAWE-EUCAR-JRC Well-to-Wheels Analysis of Future Automotive Fuels and Powertrains in the European Context [CONCAWE: Conservation of Clean Air and Water in Europe - the oil companies' European association for environment, health and safety in refining and distribution; EUCAR: European Council for Automotive R&D; JRC: European Commission Joint Research Center]) may be found at the following web addresses: <http://www.lbst.de/gm-wtw> and <http://ies.jrc.ec.eu.int/Download/eh/31>.

# A The many states of energy

“Nothing lost, nothing created,” as Lavoisier, the father of modern chemistry, wrote in his day. This motto, true as it is of chemical species, applies equally to energy. Indeed, energy is a multifarious entity, which may transform into highly diverse aspects. However, the **primary energies** that may be directly accessed in nature are limited in number: such are **fossil energies** (coal, oil, natural gas), **nuclear energy**, and **renewable energies** (hydro energy, **biomass** energy, solar energy, wind energy, geothermal energy, tidal energy). These primary energies are the constituents of what is known as the **primary energy mix** (see Figure 1).

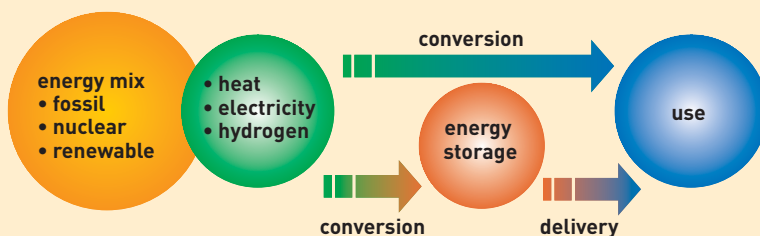


Figure 1. The energy scheme.

For most applications, energy must be **converted** to make it compatible with the use under consideration. Of course, nature, highly ingenious as it is, devised the very first **energy converters**, namely living beings. Plants, through **photosynthesis**, effect the conversion of radiant light energy into chemical energy. The human body itself allows, in particular, the conversion of chemical energy into mechanical energy, by way of the muscular system. Subsequently, humans went on to invent large numbers of converters (see Figure 2). The first such converter, chronologically, is quite simply fire, converting chemical energy (combustion) into light, and heat. Of more recent origin, a television set carries out conversion of electricity into light energy (pictures) and mechanical energy (sounds). In fact, many energy systems involve a combination of a number of converters, as e.g. a nuclear power station, effecting as it does the conversion of nuclear energy into thermal energy (reactor), then into mechanical energy (turbine), finally through to electric energy (alternator). Unfortunately, the **second principle of thermodynamics**

tells us that any energy transformation carries a cost: a more or less extensive portion of the energy involved is dissipated in the form of unusable heat (through friction in a mechanical system, for instance). In the case of a present-generation nuclear power station, the electric energy generated only amounts to one third of the nuclear energy initially contained in the fuel.

Of course, matters would be altogether too simple, however, if energy could be consumed as and when it is generated, on the very site where it is produced. In very many cases, energy-consuming sites may be far removed from the production site, production

and concomitant demand, moreover, not always being matched (as with photovoltaic electricity in nighttime, for instance). Sound energy management thus requires deployment both of an **energy distribution network**, and of **energy storage** capabilities.

**Energy transport** is effected by means of an **energy carrier**. Currently, the two main such carriers are **electricity**, and **heat**. Tomorrow, however, a new carrier may become dominant: **hydrogen**, this being converted into electricity and heat by means of **fuel cells**.

Finally, if energy is to be available at all times, it is essential that there should be the ability to store it: to “get it in a can,” so to speak. Such **storage** may take a variety of forms. Energy may be stored in **mechanical** form (*potential energy*, in the case of the water reservoir of a hydroelectric dam, or *kinetic energy*, in the case of a flywheel), or in **thermal** (hot-water tank), **chemical** (gasoline tank, primary and **storage batteries**), or even magnetic (**superconducting** coil) form.

Energy management is thus a complex, involved craft, combining production, transformation, transport, and storage. In the current context of energy debate, it is becoming increasingly apparent that, tomorrow, energy networks will grow in size and number, in accordance with a multimodal approach (concurrent management of a number of networks combining diversified energy sources). **New energy technologies** are thus bound to play an essential part in these developments.

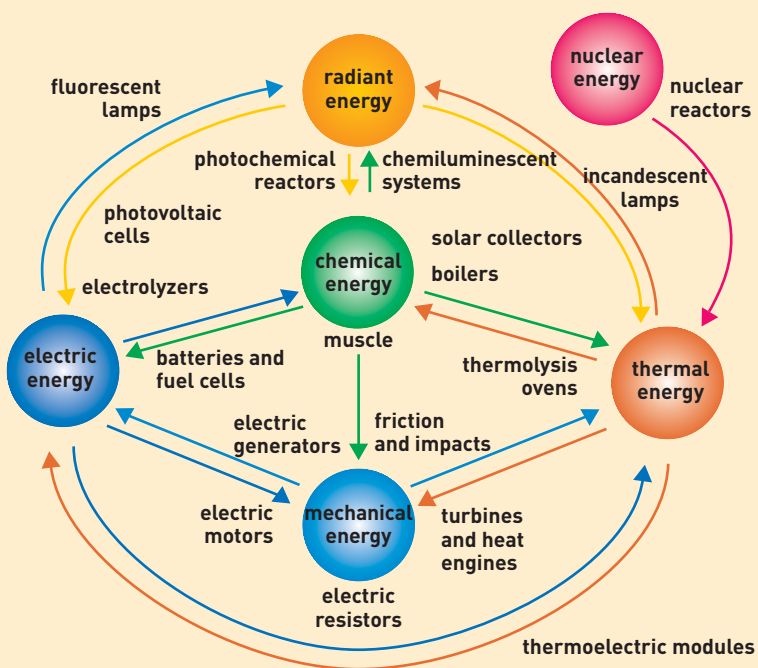
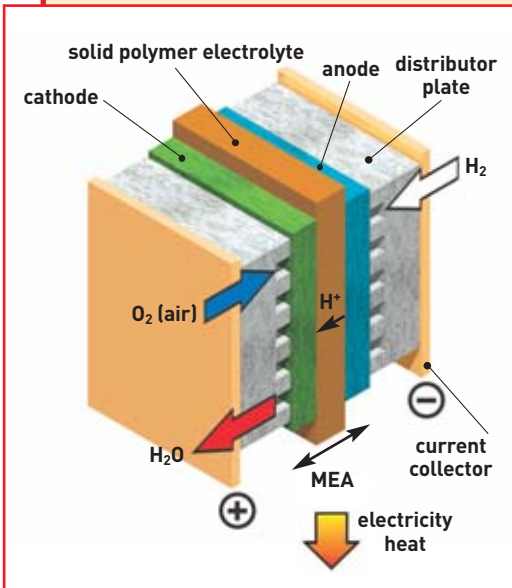


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.



**C**

# How does a fuel cell work?



Operating principle of the fuel cell: the example of the proton-exchange membrane fuel cell. MEA stands for membrane-electrode assembly.

The fuel cell is based on a principle discovered quite some time ago, since it was in 1839 that Sir William Grove constructed the first electrochemical cell working with **hydrogen** as its **fuel**, thus demonstrating the ability to generate electric current through direct conversion of the fuel's chemical energy. Since the fuel cell has the special characteristic of using two gases - hydrogen  $H_2$  and oxygen  $O_2$  - as its electrochemical couple, the **oxidation-reduction** reactions occurring inside the fuel cell are particularly simple. The reaction takes place inside a structure (the **basic electrochemical cell**), consisting essentially in two **electrodes** (the **anode** and **cathode**), separated by an **electrolyte**, i.e. a material that lets **ions** through. The electrodes employ **catalysts**, to activate, on the one side, the hydrogen **oxidation** reaction, and, on the other, the oxygen **reduction** reaction.

In the case of an acid-electrolyte cell (or **proton** exchange membrane fuel cell), the hydrogen at the anode is dissociated into protons (or hydrogen ions  $H^+$ ) and **electrons**, in accordance with the oxidation reaction:  $H_2 \rightarrow 2 H^+ + 2 e^-$ . At the cathode, the oxygen, the electrons and the protons recombine to yield water:  $2 H^+ + 1/2 O_2 + 2 e^- \rightarrow H_2O$ . The principle of the fuel cell is thus the converse of that of water **electrolysis**. The thermodynamic potential for such an electrochemical cell, consequently, stands at around 1.23 volt (V). However, in practice, the cell exhibits a voltage of about 0.6 V for **current densities** of 0.6-0.8 A/cm<sup>2</sup>. The efficiency of such a fuel cell is thus equal to about 50%, the energy dissipated naturally being so dissipated in the form of heat.

# E Storage batteries, cells and batteries: constantly improving performance

**S**torage batteries – also known as accumulators, or secondary **batteries** – and batteries – so-called primary batteries – are electrochemical systems used to store energy. They deliver, in the form of electric energy, expressed in watt-hours (**Wh**), the chemical energy generated by electrochemical reactions. These reactions are set in train inside a basic cell, between two **electrodes** plunged in an **electrolyte**, when a load, an electric motor, for instance, is connected to its terminals. Storage batteries are based on reversible electrochemical systems. They are rechargeable, by contrast to (primary) batteries, which are not. The term “battery” may further be used more specifically to denote an assembly of basic cells (whether rechargeable or not).

A storage battery, whichever technology is implemented, is essentially defined by three quantities. Its **gravimetric** (or **volumetric**) **energy density**, expressed in watt-hours per kilogram (**Wh/kg**) (or in watt-hours per liter [**Wh/l**]), corresponds to the amount of energy stored per unit mass (or per unit volume) of battery. Its **gravimetric power density**, expressed in watts per kilogram (**W/kg**), measures the amount of power (electric energy delivered per unit time) a unit mass of battery can deliver. Its **cyclability**, expressed as a number of cycles,<sup>(1)</sup> characterizes storage battery life, i.e. the number of times the battery can deliver an energy level higher than 80% of its nominal energy; this quantity is the one most frequently considered for portable applications.

Up to the late 1980s, the two main technologies prevalent on the market were lead-acid storage batteries (for vehicle start-up, backup power for telephone exchanges...), and nickel-cadmium storage batteries (portable tools, toys,

emergency lighting...). Lead-acid technology, more widely referred to as lead-acid batteries, or lead batteries, is also denoted as lead-acid systems. Indeed, the chemical reactions employed involve lead oxide, forming the positive electrode (improperly termed the cathode), and lead from the negative electrode (anode), both plunged in a sulfuric acid solution forming the electrolyte. These reactions tend to convert the lead and lead oxide into lead sulfate, further yielding water. To recharge the battery, these reactions must be reversed, through circulation of a forced current. The disadvantages found with lead-acid technology (weight, fragility, use of a corrosive liquid) resulted in the development of alkaline storage batteries, of higher capacity (amount of energy delivered during discharge), yielding however a lower electromotive force (potential difference between the system's terminals, under open circuit conditions). Electrodes for these systems are either based on nickel and cadmium (nickel-cadmium storage batteries), or nickel oxide and zinc (nickel-zinc storage batteries), or silver oxide coupled to zinc, cadmium, or iron (silver-oxide storage batteries). All these technologies use a potassium hydroxide solution as electrolyte. Lead-acid technologies, as indeed alkaline batteries, are characterized by high reliability, however gravimetric energy densities remain low (30 Wh/kg for lead-acid, 50 Wh/kg for nickel-cadmium).

In the early 1990s, with the growth in the portable device market, two new technological pathways emerged: nickel-metal hydride storage batteries, and lithium storage batteries ([see Box on Operating principle of a lithium storage battery](#)). The first-mentioned pathway, involving a nickel-based positive electrode and a negative electrode – made of a hydrogen-absorbing alloy – plunged in a concentrated potassium hydroxide solution, allowed gravimetric energy

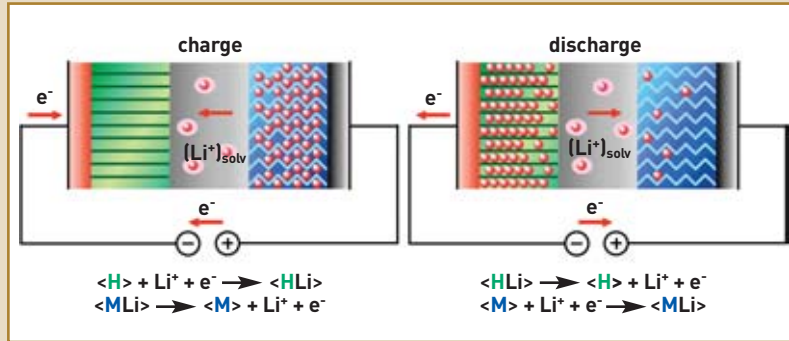
densities of 70–80 Wh/kg to be achieved. The second pathway had already been targeted by research around the late 1970s, with a view to finding electrochemical couples exhibiting better performance than the lead-acid or nickel-cadmium storage batteries used up to that point. Initial models were thus designed around a metallic-lithium-based negative electrode (lithium-metal pathway). However, that technology was faced with issues arising from poor reconstitution of the lithium negative electrode, over successive charging operations. As a result, around the early 1990s, research was initiated on a new, carbon-based type of negative electrode, this serving as a lithium-insertion compound. The lithium-ion pathway was born. Japanese manufacturers soon made their mark as leaders in the field. Already in business as portable device manufacturers, they saw the energy source as numbering among the strategic components for such devices. Thus it was that Sony, not initially involved in battery manufacture, decided, in the 1980s, to devote considerable resources to advance the technology, and make it suitable for industrialization. In February 1992, Sony announced, to general stupefaction, the immediate launching of industrial production of lithium-ion storage batteries. These early storage batteries exhibited limited performance (90 Wh/kg). Since then, these batteries have seen notable improvement (from 160 Wh/kg to over 180 Wh/kg in 2004), owing, on the one hand, to the technological advances made (reduction in the unproductive fraction of battery weight and volume), and, on the other, to optimization of materials performance. Gravimetric energy densities of over 200 Wh/kg are expected around 2005.

<sup>(1)</sup> One cycle includes one charge and one discharge.

## Operating principle of a lithium storage battery

During use, hence during discharge of the **storage battery**, lithium released by the **negative electrode** (<H>: host intercalation material) in **ion** form ( $\text{Li}^+$ ) migrates through the ion-conducting **electrolyte** to intercalate into the **positive electrode** active material (<MLi>: lithium-insertion compound of the metal oxide type). Every  $\text{Li}^+$  ion passing through the storage battery's internal circuit is exactly compensated for by an **electron** passing through its external circuit, thus generating a current. The **gravimetric energy density** yielded by these reactions is

proportional both to the difference in potential between the two electrodes, and the quantity of lithium intercalating into the insertion material. It is further inversely proportional to system total mass. Now lithium is at the same time the lightest (molar atomic mass: 6.94 g), and the most highly **reducing** of metals: electrochemical systems using it may thus achieve voltages of 4 V, as against 1.5 V for other systems. This allows lithium batteries to deliver the highest gravimetric and volumetric energy densities (typically over 160 Wh/kg, and 400 Wh/l),



50% greater, on average, than those of conventional batteries. The operating principle of a lithium storage battery remains the same, whether a lithium-metal or carbon-based negative electrode is employed. In the latter case, the technological pathway is identified as lithium-ion, since lithium is never present in metal form in the battery, rather passing back and forth between the two lithium-insertion compounds contained in the positive and negative electrodes, at every charge or discharge of the battery.



## B The greenhouse effect and CO<sub>2</sub>

The Sun's energy reaching the ground warms the Earth, and transforms into **infrared radiation**. Just like the panes of a greenhouse – hence the name given to this mechanism – some of the gases present in the atmosphere trap part of this radiation, tending to warm the planet. Thus, in terms of power, the Earth receives, on average, slightly less than 240 **watts/m<sup>2</sup>**. Without the **greenhouse effect**, mean temperature on Earth would stand at  $-18\text{ }^{\circ}\text{C}$ , and very little water would be present in liquid form. This effect thus has a beneficial influence, since it allows our planet to experience a mean temperature of  $15\text{ }^{\circ}\text{C}$ .

However, from the beginning of the industrial era, i.e. for more than a hundred years, humans have been releasing into the atmosphere gases (**carbon dioxide**, **methane**, **nitrogen oxides**, etc.) that artificially augment the greenhouse effect. Since 1750, this increase, with respect to “well-mixed” gases, has amounted to  $2.43\text{ W/m}^2$ . Contributing as it does an “additional radiative forcing” of  $1.46\text{ W/m}^2$ , carbon dioxide (CO<sub>2</sub>) accounts for more than half of this “additional greenhouse effect,” well ahead of methane ( $0.48\text{ W/m}^2$ ), **halocarbons** [chlorofluorocarbons [CFCs], hydrochlorofluorocarbons [HCFCs], and hydrofluorocarbons [HFCs]), accounting for  $0.34\text{ W/m}^2$ , and nitrogen dioxide ( $0.15\text{ W/m}^2$ ). Further, the **ozone** in the troposphere exhibits a *positive* radiative forcing of  $0.35\text{ W/m}^2$  (however, it is estimated that depletion of the stratospheric ozone layer observed between 1979 and 2000 has resulted in a *negative* radiative forcing, of  $0.15\text{ W/m}^2$ ).

This addition to the natural greenhouse effect ( $155\text{ W/m}^2$ ) is small, correspon-

ding to an increase of about 1%. Nevertheless, it is practically certain that this has contributed to the rise in mean temperature, for our planet, of about  $0.5\text{ }^{\circ}\text{C}$ , observed over the 20th century (see Figure 1). If nothing is done to curb these emissions, carbon dioxide concentration in the atmosphere (see Figure 2) could double by 2100. From current world consumption <sup>(1)</sup> of **fossil** fuels (7,700 Mtoe), the mass of CO<sub>2</sub> currently produced may easily be computed: 20 billion tonnes per year!

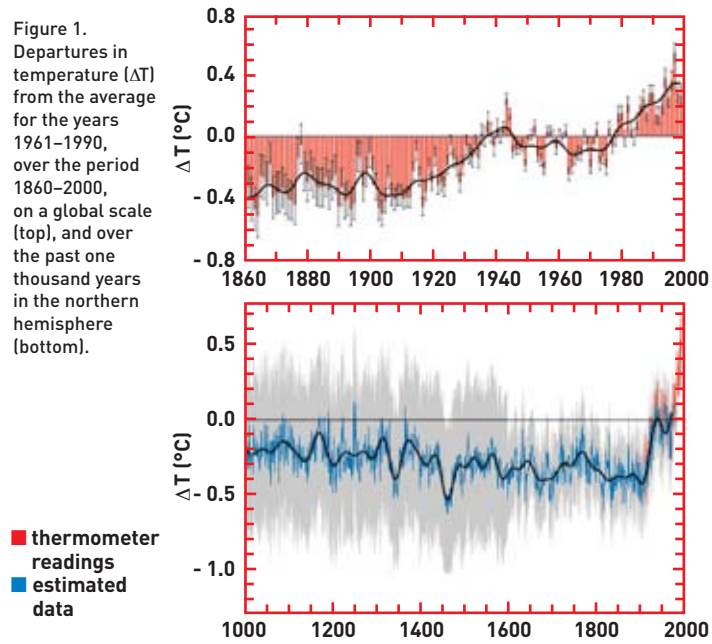
This could result in a substantial increase in the greenhouse effect, causing, through nonlinear amplifying effects,

(1) European Community, Directorate General for Energy (DG XVII), “Conventional Wisdom” scenario (*European Energy to 2020: A scenario approach*, 1996).

profound alterations in climate. Most models predict that doubling the present carbon dioxide concentration would result, by the end of the 21st century, in a rise in temperature of some  $2\text{--}3\text{ }^{\circ}\text{C}$ . Some models even yield a bracket of  $1.5\text{--}4.5\text{ }^{\circ}\text{C}$ , meaning dramatic consequences could be foreseen for the environment, such as a substantially rising sea level.

Such figures may seem small, entailing only minor consequences for the climate; that, however, is not the case. To understand this point, one should bear in mind that during the “little ice age,” from 1450 to 1880, mean temperature only fell, in France, by  $1\text{ }^{\circ}\text{C}$ , on average. Some 6,000–8,000 years ago, as Western Europe experienced a war-

Figure 1. Departures in temperature ( $\Delta T$ ) from the average for the years 1961–1990, over the period 1860–2000, on a global scale (top), and over the past one thousand years in the northern hemisphere (bottom).



## B The greenhouse effect and CO<sub>2</sub>

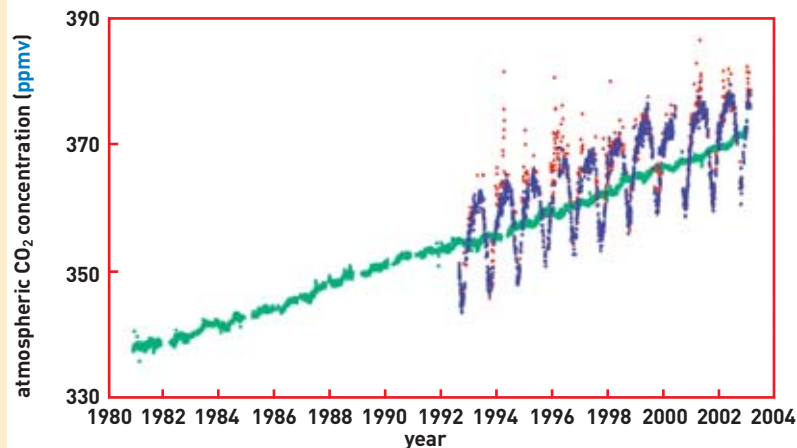


Figure 2.

Evolution of atmospheric CO<sub>2</sub> concentration since 1980, as measured on a daily basis by the automatic stations of the Climate and Environmental Science Laboratory (LSCE: Laboratoire des sciences du climat et de l'environnement), since 1981 on Amsterdam Island (Indian Ocean), and since 1992 at Mace Head, on the western coast of Ireland.

Readings on Amsterdam Island (shown in green), well away from any direct perturbation of human origin, essentially evidence the constant rise in concentration. The Mace Head site basically measures oceanic atmosphere (under normal conditions, westerly winds: blue). When wind conditions are reversed, the site receives a continental atmosphere, showing a strong excess in CO<sub>2</sub> (red plots), compared to oceanic atmosphere. Over the mean rise in CO<sub>2</sub> concentration is superimposed a marked seasonal modulation, due to plant vegetative cycle (chlorophyll photosynthesis), plants being CO<sub>2</sub> emitters in winter, and CO<sub>2</sub> absorbers in summer.

mer spell, with a mean temperature 2–3 °C higher than it is today, the Sahara was not a desert, but a region of abundant rainfalls. It is not so much the rise in temperature that gives cause for concern, as its rapid variation (in the course of one century). The large variations previously observed in nature all occurred over much longer timescales, for those at least of a global character. Thus, the last glaciation lasted 100,000 years, and the corresponding deglaciation took 10,000 years. The rapid variation we are currently experiencing may induce major, unexpected perturbations in the climate and the ecosystem, which will not always have time to adapt.

### From Rio to Kyoto: the major conferences on the global environment

The evolution of the global environment has led to major conferences being organized, starting in the closing decade of the 20th century.

At the Earth Summit, held in **Rio de Janeiro** (June 1992), the United Nations Framework Convention on Climate Change was signed, this setting the goal of a stabilization of **greenhouse gas** emissions (this convention came into force on 21 March 1994).

At the Kyoto Conference (December 1997), the protocol was signed providing for a global reduction in emissions of such

gases, by an average 5.2% in the period 2008–2012, compared to 1990 levels, for **OECD** countries and Eastern European countries (including Russia). Reduction targets for the **European Union** and France are set at 8% and 0% respectively. The ways and means to meet these targets were debated, unsuccessfully, in November 2000 at **The Hague**. Subsequent conferences, held in **Marrakech** (2001), **Johannesburg** (Earth Summit held in August–September 2002), **New Delhi** (October 2002), **Moscow** (September–October 2003), and **Milan** (December 2003) had still not enabled, by 2004, this **Kyoto Protocol** to be brought into force, until Russia finally decided to ratify the document, at last allowing this enforcement in February 2005.

Under the impetus provided by the United Nations Environment Program (**UNEP**), the issues raised by substances that deplete the ozone layer in the atmosphere were addressed in **Vienna** (1985), and most importantly in **Montreal** (1987), where the protocol was signed, imposing a reduction in production and use



The Mace Head monitoring station, Ireland.

of chlorofluorocarbons (CFCs). This protocol was specified by amendments adopted in **London** (1990), imposing a ban on CFCs from 1 January 2000, and extending controls to other compounds (including HCFCs), **Copenhagen** (1992), **Montreal** (1997), and **Beijing** (1999).