



## Fuel production by thermochemical transformation of biomass

The expertise achieved by CEA research workers in thermalhydraulics and thermochemistry, as in process management and optimization, may prove decisive as regards carrying through the development of the technologies required for the thermochemical transformation of biomass.



Analysis of product gases at the outlet of the experimental reactor set up at CEA/Grenoble for investigation of steam biomass gasification on a high-temperature (800-1,000 °C) fluidized bed, for the purposes of synthesis gas and biofuel production. This reactor allows characterization of efficiency, and to gain knowledge as to management and control of this type of device, and further allows testing of technological components (biomass feed and filtration).

At a time when industrial society is beginning to anticipate the end of relatively cheap oil, and collective awareness is emerging, in support of countering the **greenhouse effect** (see **Box B**, The **greenhouse effect and CO<sub>2</sub>**), the use of **biomass** and waste as an energy source, or to provide **hydrogen** and **biofuels** stands as a particularly attractive alternative, holding out major stakes for the future. The expertise available at CEA in the fields of **thermal-hydraulics** and **thermochemistry**, as in the areas of process management and optimization, are decisive assets when it comes to carrying out the development and transfer to industry of the required technologies.

### The challenges

Biomass includes all plants that grow on the face of the Earth. It effects the capture and storage of solar energy, which may then be recovered in the form of **fuels**, including **hydrocarbon fuels**, with no impact on the greenhouse effect, through transformations of varying effectiveness, in terms of energy and economics. Four main paths may be considered:

The first one, *combustion* (or incineration), essentially yields heat at a temperature, around 650 °C, that is restricted owing to presence in the smoke of nitrogen, carried along in the air, and acid fumes or condensa-

ble tars,<sup>(1)</sup> causing corrosion processes. In such conditions, **cogeneration** of electricity and heat, by means of a steam cycle, only brings a yield of 30% electricity and 70% heat, the latter representing a complement that is economically difficult to use to generate added value.

The second path is *methanation*, carried out through **anaerobic** digestion - i.e. decomposition by bacterial agents in the absence of air - of high-moisture materials, such as algae, animal manure, or household waste. It is possible to obtain in this manner a gaseous mixture of **methane** (50-60%) and **carbon dioxide** (35-40%), making for complications as regards utilization, restricted to *in-situ* combustion for generation of heat and electricity.

A third path, *alcohol fermentation*, is suited to sugar crops such as beet or sugarcane (sacchariferous produce), or starch crops such as cereals (amylaceous produce). After hydrolysis and preparation of a sugar solution, subjected to fermentation, **ethanol** is obtained by **distillation**. Overall efficiency is penalized by the high energy consumption associated to crop cultivation and the distillation operation.

Finally, *thermochemical transformation*, resulting in gasification of organic and plant materials, is particu-

(1) Tars: oily, viscous, and brown or black in color, tars are byproducts from the distillation or charring of coal or wood.

larly suited to lignocellulosic <sup>(2)</sup> materials such as wood or straw, as regards yielding added value. This pathway offers the strongest potential, in energy terms, for the manufacture of hydrocarbon fuels.

As far as mainland France is concerned, the usable lignocellulosic resource could provide up to 10% (20 Mtoe/year) of current **primary energy** consumption. This usable resource includes a proportion of forestry products, but equally agricultural products, dedicated energy crops and some wastes (common industrial residues, household waste). This would entail collecting waste products from forestry (residuals) and harvesting now-abandoned coppices, prejudicial as these are to forest productivity. It would equally involve taking in agricultural residues (straw) which, at present, are destroyed to a needlessly high extent by burying. This would also mean devising the right way of turning to profitable use the 15% of agricultural land not serving for food production, through cultivation of herbaceous or lignocellulosic energy crops suited to soil type and climate. Finally, it will be essential to improve the quality of sorting practices, to ensure better revenue from biomass, returning as it does as end-of-cycle waste (wood, paper, cardboard...). This twofold economic stake, of clean hydrocarbon fuel production and enhanced revenue from waste, stands as a definite challenge for society, in the decades to come. Which is why CEA has deemed it necessary to commit its expertise to contributing to the quest for the best-suited solutions (see Box 1).

### Technological barriers

Technological barriers arise at various levels. Biomass gasification, as indeed coal gasification, is no recent capability. It was used, most notably, in the years before and after the Second World War, to compensate for the scarcity of petroleum products. It was abandoned, however, as soon as **fossil** hydrocarbon fuels once more became cheaply available. Thus it is not the feasibility of gasification that needs to be demonstrated so much as its improved reliability and enhanced economic viability, on the basis of the new givens, corresponding to the end of relatively cheap oil, the taking on board of the effort to counter the greenhouse effect, and the need to generate employment, particularly in the countryside.

Among the barriers on which CEA's expertise may be expended, three appear as crucial. They condition an installation's operating costs, or impair its viability.

The first barrier concerns the price of raw materials, this being heavily impacted by the collection, storage and transport difficulties in agricultural and forestry contexts. To achieve lower costs, constraints as to the kind of material, and material homogeneity, may be relaxed, in particular by allowing simultaneous processing of "clean" biomass along with waste for which

(2) Lignocellulosic produce: consisting of lignin and cellulose. Lignin is a complex organic substance, the main constituent in wood, which pervades cells, fibers and conduction channels, rendering them impervious, inelastic and rigid. Cellulose is a macromolecular compound, one of the sugar (saccharide) group, a glucose polymer, and an essential, characteristic constituent of the plant cell wall.

## An extensive network of collaborations

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Throughout the program, collaborations are to be set up with an extensive network of French or European partners. As regards the area of basic knowledge, relationships have been initiated with a number of public-sector and academic research groups. Tar analysis is carried out with GRECA (Groupe de recherche sur l'environnement et la chimie atmosphérique: Research Group on the Environment and Chemistry of the Atmosphere), at Joseph-Fourier University, Grenoble (France). Other aspects are taken up with **CNRS** units (pyrolysis and gasification, with the Albi mine engineering school; fluidized bed modeling, with the Catalytic Process Engineering Laboratory in Lyons). Manufacturers having the capability, ultimately, to build facilities are invited from the start to contribute to the setting up and subsequent progress of the program. As regards prospecting for, and provision of, resources, agricultural producers coming under the aegis of the Association générale des producteurs de blé (AGPB: General Wheat Producers' Association) and Institut technique des céréales et fourrages (Technical Cereal and Fodder Institute - now part of Arvalis-Institut du végétal) are involved (see Box 4). Finally, concerning lignocellulosic resources, departments coming under the French Ministry of Agriculture and Forestry are involved, along with major sawmills. Relationships have also been set up internationally, in particular with manufacturers and academics in Denmark, a country pursuing a highly proactive policy in the area of renewable energies. A further cooperation of note is set up with **CIRAD** (Centre de coopération internationale en recherche agronomique pour le développement: French International Cooperation Center for Agricultural Research for Development)

such disposal is economic. For that purpose, sufficiently flexible technologies must be developed, and a precise understanding gained as to the thermal and chemical behavior of the materials to be transformed. The second barrier concerns *transformation efficiency*, which determines the amount of material to be used to yield a given amount of energy. Optimization of facility operation calls for experimental research to enable a model of the entire process to be arrived at and undergo qualification, which will subsequently assist in the design and operational control of high-performance units. Three crucial operations should, in this respect, be investigated and analyzed separately (see Box 2): **thermolysis, gasification, and tar and ash removal**. Only by means of a detailed, exacting analysis of the various materials that may be used, and of the numerous thermochemical operations to be carried out will it be possible to devise suitable technologies, and further optimize and manage the gasification plants that will enable production of the renewable fuels of tomorrow.

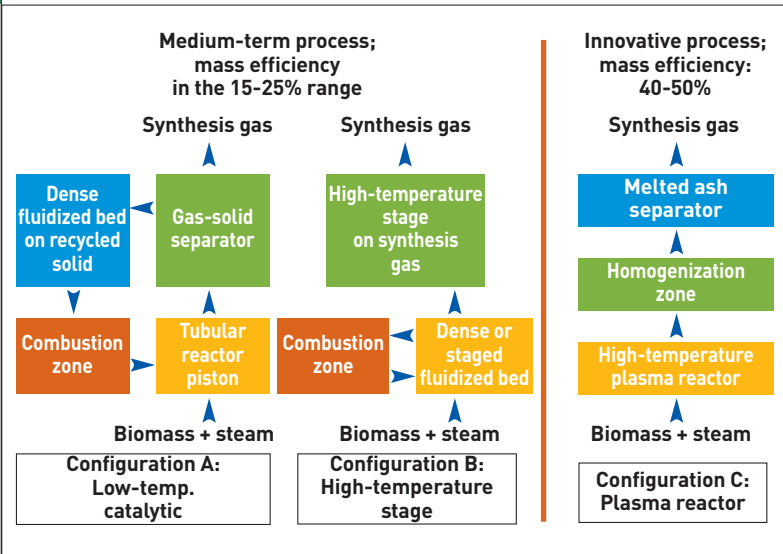


Figure 1. Biomass gasification processes selected at the outcome of the study conducted by CEA and IFP.

## Process selection in collaboration with IFP

As part of a collaboration with IFP initiated in 2002, an exhaustive analysis of existing processes was carried out, resulting in a number of processes being put forward (see Figure 1):

- a process that could be implemented in the short term (~ 10 years), based on a low-pressure fluidized bed technology. The energy required for the transformation would be generated by combustion of part of the biomass. This technology allows a fuel mass efficiency<sup>(3)</sup> of the order of 15% to be achieved. By adding a high-temperature stage, this efficiency could rise to 20-25%. In the latter case, outside energy would have to be supplied to the high-temperature stage;
- a process that would require more extensive technological development, based on a plasma or arc oven technology. The required energy would then be wholly

(3) Mass efficiency is defined here as the oil equivalent mass generated per kilogram of dry biomass input into the process. Fuel mass efficiency concerns fuel manufactured by that process.

## A succession of intricate, controlled operations

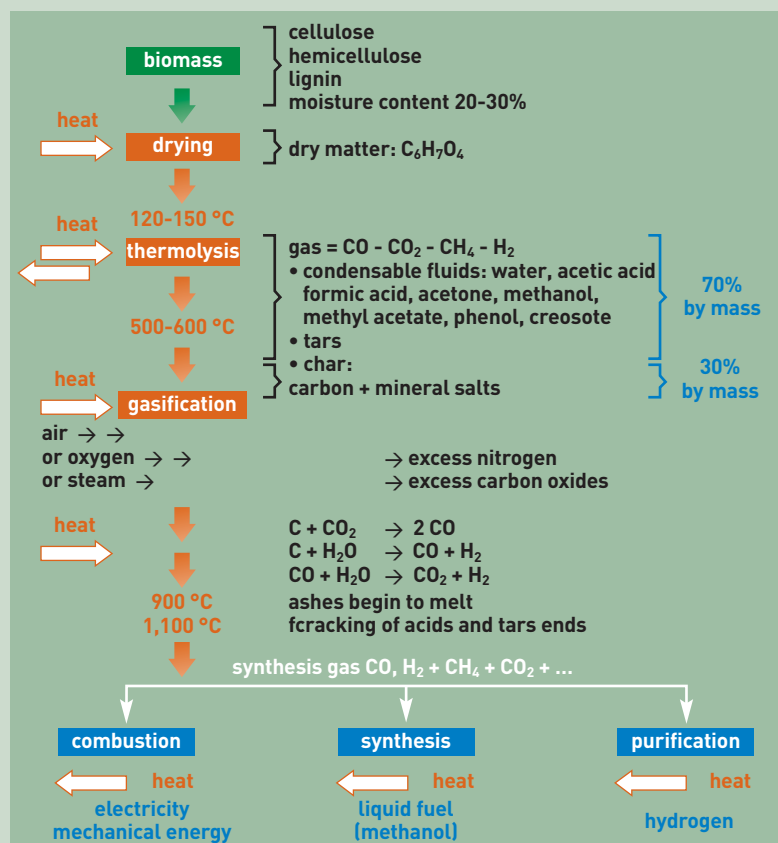
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The thermochemical path, comprising biomass thermolysis and gasification (see Figure), involves a succession of operations requiring at the same time transfer of large amounts of heat and control of the proportion and contact time for the reactants present.

After the drying operation, which is highly endothermic, thermolysis consists in the thermal degradation of products which, at around 600 °C, have lost 70% of their mass to the gaseous state, while 30% of the original mass stays solid, accounted for by char, essentially consisting in carbon (C). Carbon gasification is continued up to around 900-1,000 °C through action of a reactant such as air, oxygen (O<sub>2</sub>) or steam (H<sub>2</sub>O), effecting the more or less complete oxidation of carbon into carbon monoxide (CO) or carbon dioxide (CO<sub>2</sub>). Use of air, for this step, is inexpensive; however, it does carry into the end product some undesirable nitrogen. Oxygen, obtained through distillation of air, is expensive, and hazardous. Use of air or oxygen favors formation of carbon oxides. Using steam as a reactant, an additional quantity of hydrogen (H<sub>2</sub>) is recovered. However, an auxiliary heating method must be employed, e.g. combustion of residual carbon or purge gas, or an outside energy supply brought in.

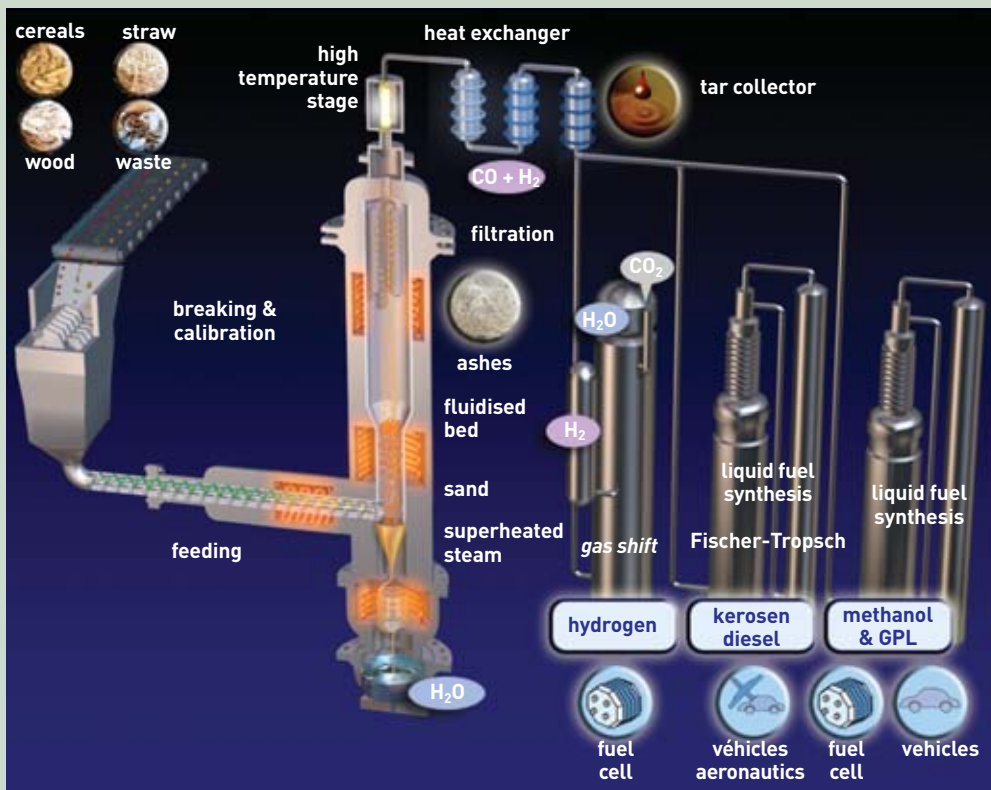
Obtaining a high-grade, noncorrosive gas requires removal of the acids and tars yielded by thermolysis. For that purpose, these products must be brought to some 1,200-1,300 °C (high-temperature stage) to effect their thermal degradation (cracking), or a catalyzed reaction must be carried out at 800-900 °C, to preclude ash fusion and clinker<sup>(1)</sup> formation, which is found to occur at 900-1,000 °C. Use of a high-temperature stage further allows reforming of methane (CH<sub>4</sub>) into CO and H<sub>2</sub> to be carried out concurrently. The gas obtained may be burned in an engine or a gas turbine to generate mechanical energy or electricity. It may also lead on to synthesis of hydrocarbons (Fischer-Tropsch diesel fuels,

(1) Clinker: combustion residue, in particular from coal or wood combustion, resulting from the melting and solidification of the mineral salts making up the ashes.



methanol, dimethyl ether...), directly usable as liquid hydrocarbon fuel or energy carrier, or as chemical feedstock. Finally, biomass gas may be refined to extract its hydrogen, this providing, by way of this path, the clean, renewable fuel required for fuel cells.

An important point is that the same amount of carbon dioxide is released, whether it be by the slow oxidation of wood left in the open (rotting) or by rapid oxidation in a (good) energy-generating combustion. As this amount of carbon gas is what the plant used for its own growth, the net outcome is perfectly neutral in terms of the environment and greenhouse effect impact.



Fluidized-bed thermochemical process for the transformation of biomass into fuel investigated at CEA/Grenoble.

In a **fluidized-bed** reactor, steam gasification of solid **thermolysis** residues, essentially carbon (C) and 5-10% of mineral salts, is carried out at around 800-900 °C in well controlled temperature homogeneity and reactant proportion conditions. The so-called gas-water shift, an **endothermic** reaction occurring between carbon and steam (H<sub>2</sub>O), yields a mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>), known as **synthesis gas**. The requisite reaction heat is provided by a heat-transfer fluid passing in cocurrent or countercurrent flow between the gasification reactor, where it is dispersed to ensure a homogeneous heat supply, and an entrained-bed heating oven, where it is brought to about 900 °C by

atmospheric combustion of residues extracted from the process (dust and solid, non-gasified particulates, or purge gas such as e.g. excess carbon monoxide or **methane**). Setting maximum temperature at 900 °C precludes ash fusion and clinker <sup>(1)</sup> formation, liable to impede particulate motion. The choice for heating fluid of a calcium- and magnesium-rich material, such as dolomitic sand, carries the benefit of a **catalyzing** effect for gasification and tar-removal reactions, which are thus effected over a shorter time, or at lower temperature.

(1) See note in Box 2.

supplied from outside sources. High mass efficiencies could thus be achieved, in the 30-40% bracket. On the basis of an annually renewable biomass inventory of some 50 million tonnes, the latter process would allow production equivalent to some 15-20 Mtoe, i.e. 30-40% of the fuel consumed for transportation purposes in France, currently manufactured from imported petroleum. Within certain limits, a fossil energy supply may be used; however, if mass efficiency is to double, the outside energy supply may not, of course, be of fossil origin. The only energy available for mass consumption, while remaining free from greenhouse effect impact, is nuclear energy. Estimated production costs would lie in the range €0.4-0.7/liter diesel equivalent, depending on the process chosen, facility size, raw material costs and the cost of the additional energy required.

### Expertise in essential areas

CEA and IFP can avail themselves of expertise and experimental facilities in such essential areas as thermal processing of plant or organic materials and residues, and the design, modeling and optimization of industrial units and processes involving chemistry, thermics, and thermalhydraulics. Since the middle of 2001, characterization campaigns have been conducted at the Cadarache site. Initially, these were concerned with wood, straw or grain (cereal) thermolysis, but equally with thermolysis of animal protein or bone meal and sludge from urban wastewater treatment plants, or paper, cardboard and other nonrecyclable residues. The teams charged with nuclear reactor design are also bringing to bear, at the Grenoble



site, in collaboration with IFP teams based at Solaize, their expertise in the analysis and modeling of thermic and thermalhydraulic processes, to achieve improved understanding and knowledge of basic processes, such as the fluidized-bed gasification (see Box 3) and steam gasification of carbonaceous residues.

Three main goals have been set for the years to come. The first concerns design, and mastery, of the key component that is the *fluidized-bed or plasma reactor*. The second, more encompassing, goal concerns *modeling the process as a whole*, in order to make available tools which may serve both as decision aids, as regards choice of products for gasification, and as design or optimization resources for future installations. The third goal will be demonstration of process feasibility on an *experimental platform*, with a transformation capacity of several hundred kilograms biomass per hour.

### An abundant hydrogen source for fuel cells

Biomass, as a form of transformed solar energy, has the capacity to cover a major part of the energy consumption of a country such as France, in sustainable fashion (see Viewpoint below). The energy required to obtain one mole of hydrogen from biomass is of the order of 60 kJ. This energy is comparable to that

required for steam methane **reforming** (~ 40 kJ), and much lower than that required to split a molecule of water into hydrogen and oxygen (~ 280 kJ). Biomass thus represents an attractive source as regards hydrogen production. CEA is taking part in the European Union's Green Fuel Cell Program and is to conduct trials, for this program, as to the possibility of using biomass-derived **synthesis gas** to feed an SOFC **fuel cell**.

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## Viewpoint

### An historic opportunity, according to wheat producers

**Fuel production from agricultural biomass represents "an historic opportunity," according to the French General Wheat Producers' Association (APGB).**

The French agricultural landmass currently holds a reserve of "set-aside" land of 1.5 million hectares. This area could double over the next five years, in spite of spiraling urban-development land use and the growth of other extraneous holdings alienated from biomass production, according to the French General Wheat Producers' Association (APGB: Association générale des producteurs de blé). Pierre Gatel, a consultant at APGB, considers that "development of energy applications for agricultural biomass is currently limited. Within five years, rational cultivation of this land would enable going from a cover of under 1% **bio-fuels** in 2003 to 5.75% of transportation energy consumption." This target is the one put forward by European governments, in the context of two European Directives, of which the first one, promoting use of biofuels, has already been passed, and the second, concerning specific biofuel taxation, is on its way to adoption. "Of all alternative fuels (LPG, VNG, electricity, etc.),

biofuels are those getting, per unit energy consumed, the least public support," APGB points out, adding that "**ethanol**, used in the form of **ETBE** fuel, is subjected in 2003, per gigajoule, to taxation comparable to that affecting diesel fuel, i.e. over four times that for LPG or vehicular natural gas."

According to Pierre Gatel, "the motivations that got Europe 'moving' as regards biofuels are of two kinds: the drive to counter climate change, and seeking to reduce dependence. The same motivations are currently involved in the choice of a new French national policy favoring transformation of renewable resources of local origin.

"Such an option is, on the one hand, required if renewable immediate-use fuels are to be brought into operation. And, on the other hand, in the context of focused research choices to improve the economic efficiency of production of biocomponents usable for fuel purposes, it is essential to prioritize an orientation along which the research work currently being carried out by CEA, IFP,

and Arvalis-Institut du végétal represents the first concrete step."

"Existence of an agriculture with readily-accessed resources, with the ability to respond flexibly to the twofold energy and food demand, is a relatively recent opportunity. This opportunity is enhanced by availability, equally instantly, of the requisite collaborations and multidisciplinary expertise (in genetics, agronomy, energetics...) to achieve such added value for biomass."

"It is thus to be hoped for that innovative research directions, such as those explored by CEA, will prove attractive to decision-makers. They will enable a very gradual drawing away from absolute dependence on oil imports for transportation purposes. Achieving this while combining countering the greenhouse effect with securing enhanced revenue for the nation's soil resources represents an historic opportunity, such as that, 40 years ago, which led the country to develop its nuclear power program, and which has already resulted in greater independence."

# 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).

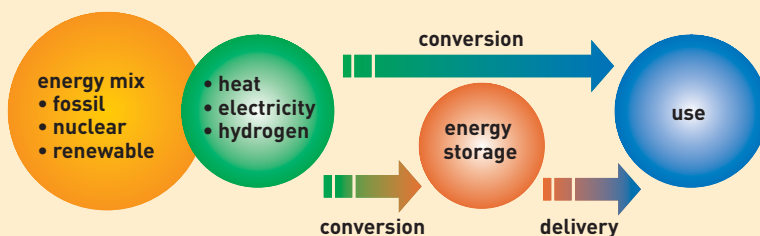


Figure 1. The energy scheme.

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.

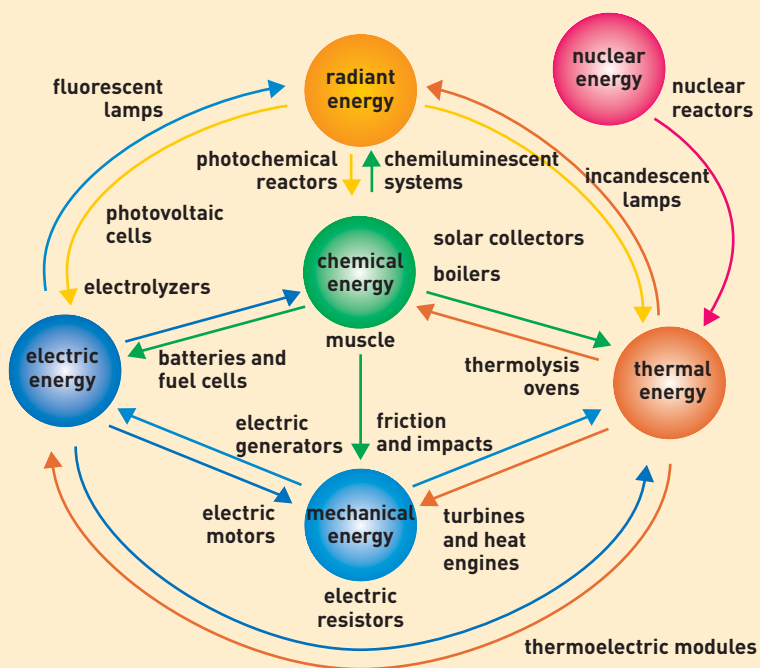
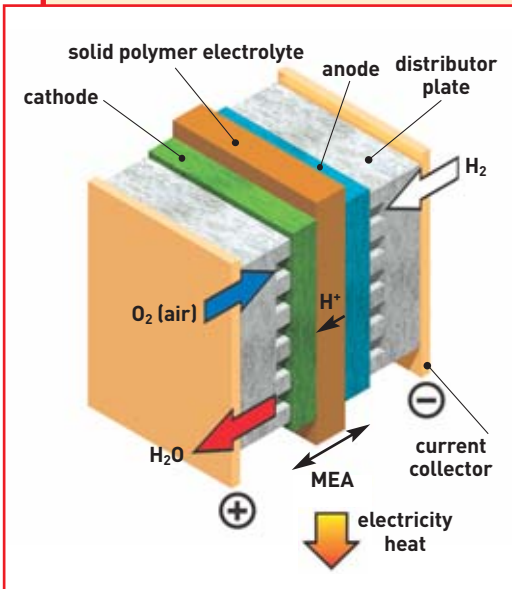


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.

**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.

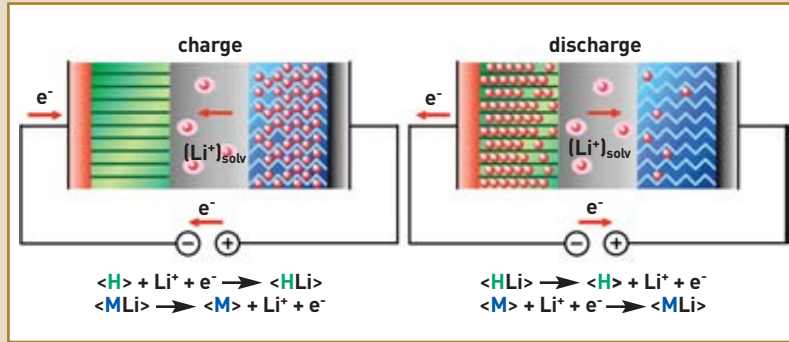
<sup>(1)</sup> One cycle includes one charge and one discharge.



## 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!

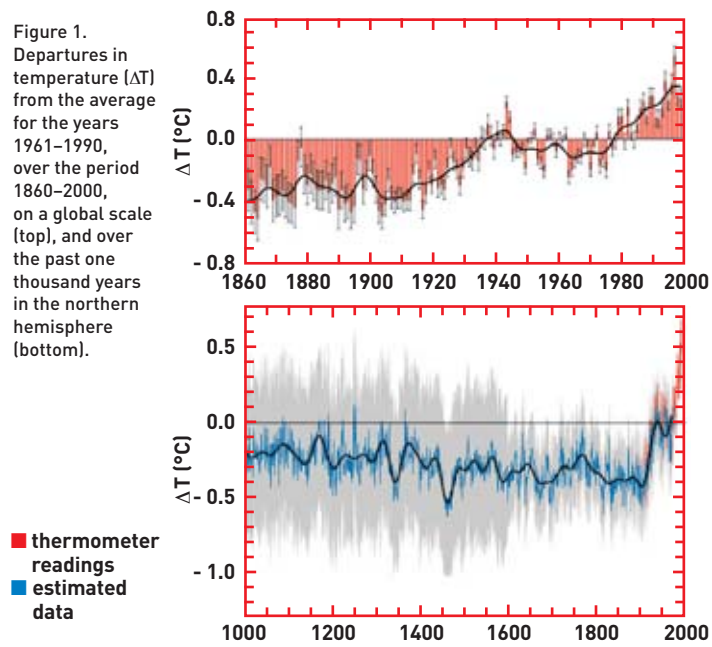
This could result in a substantial increase in the greenhouse effect, causing, through nonlinear amplifying effects,

(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>

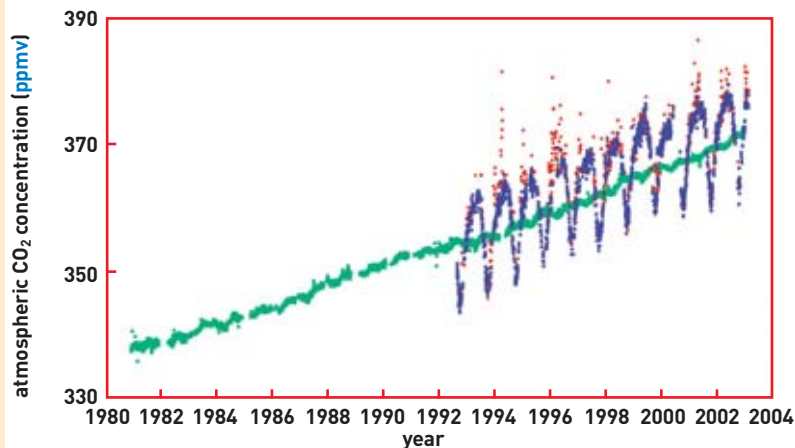


Figure 2.

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).