Challenges in Using CO_2 as a Feedstock for Chemicals and Fuels

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χ Physique χ Analytique Paris Centre ED 388

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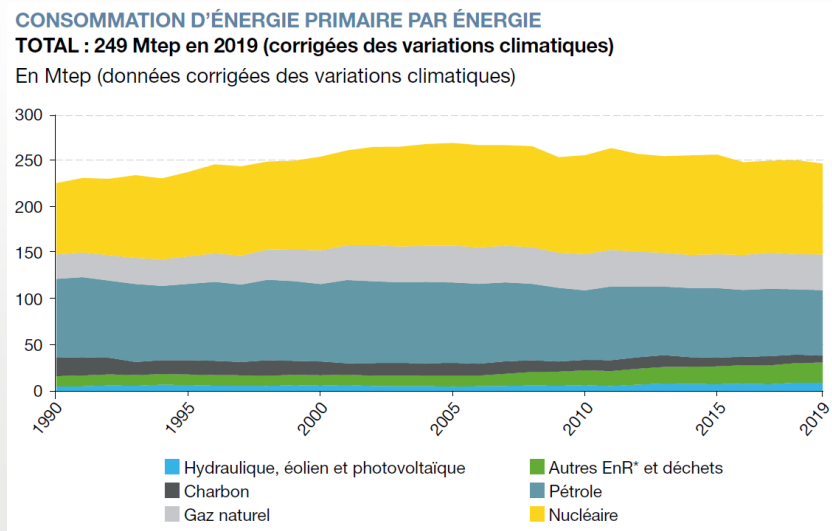
Vendredi 2 Avril 2021

ENERGY CONSUMPTION IN FRANCE

Global consumption decreases since 2005.

Since 1990:
- ✓ **Coal -63%**
- ✓ **Oil -17%**
- ✓ **REn x2**

but
- ✓ **Natural gas +46%**
- ✓ **Electricity +28%**

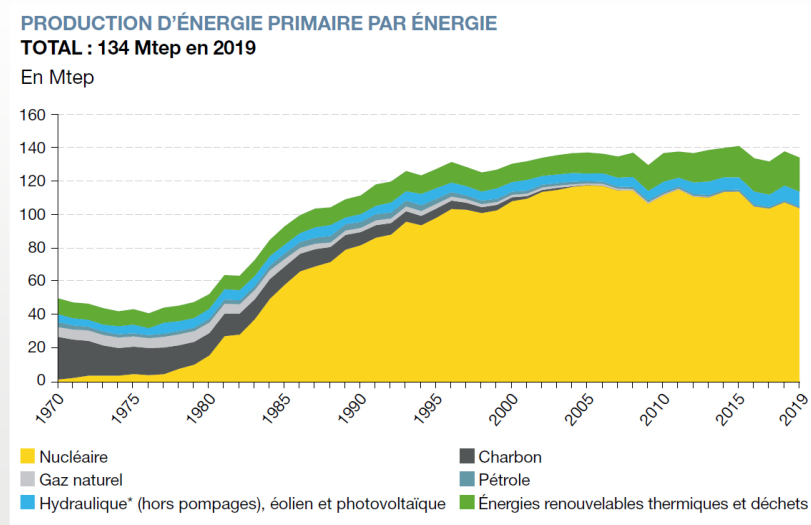


ENERGY SOURCES IN FRANCE

Energy production (2019) :
- ✓ **77% nuclear**
- ✓ **20% renewable (wood, hydraulic, wind)**

but
- ✓ **<1% oil**
- ✓ **0% natural gas**
- ✓ **0% coal (still 5 power plants in Metropolitan France)**

= huge importations of fossile energy sources



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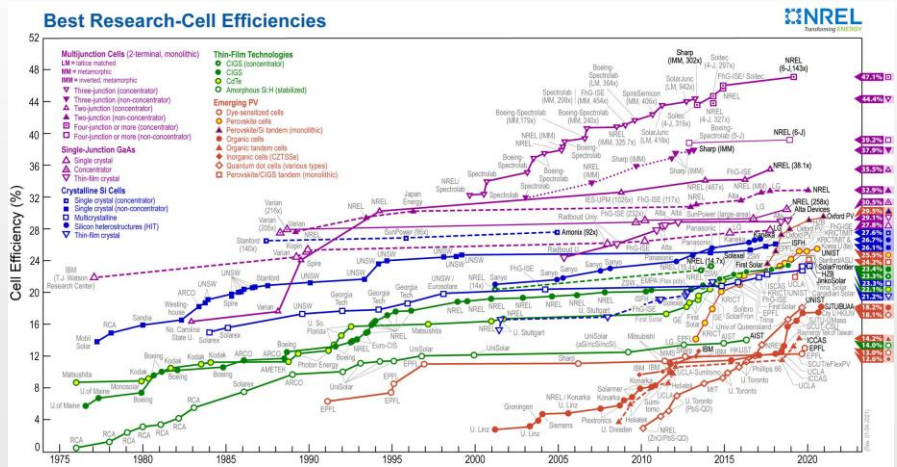
THE SUN: INEXHAUSTIBLE SOURCE OF ENERGY!

10% solar energy conversion using 0,3% Earth continental surface could satisfy world energy demand expected in 2050…

Solar energy reaching Earth…in 1 hour is equivalent to the world energy consumption… in 1 year



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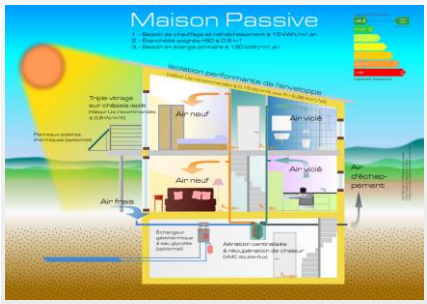
HOW TO RECOVER SOLAR ENERGY?

3 ways of recovering solar energy:

- ✓ **photovoltaic: solar panels transform % of the radiation received into electricity,**
- ✓ **passive: building a well-oriented and -insulated house provides most of the heating,**
- ✓ **thermodynamic: focused solar light heats a fluid that drive a turbine to produce electricity.**



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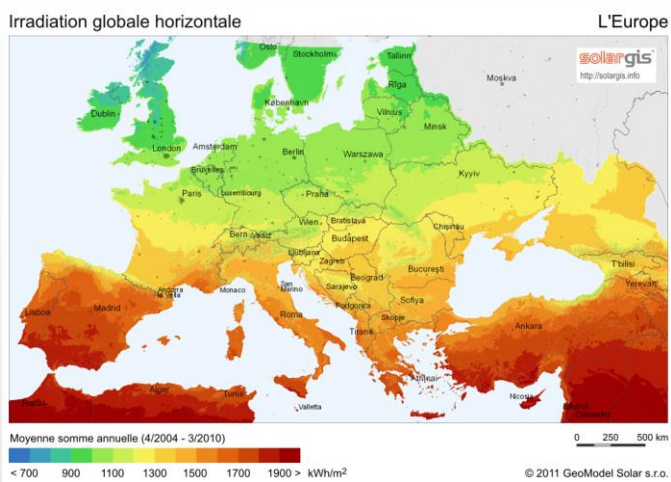
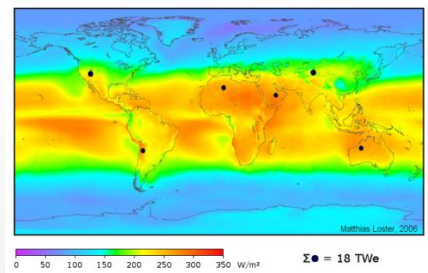
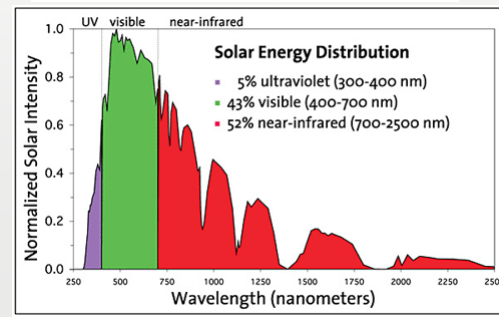
WHAT WE RECEIVE FROM THE SUN







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SUNLIGHT IS *NOT* A CONSTANT FLUX

Solar energy reaching a specific location on Earth depends on:

- ✓ **energy flow** from the Sun (decadal fluctuations, seasons, ponctual),
- ✓ **nebulosity** (clouds, fog, aerosols, etc.), which is strong at the equator and weaker in intertropical areas,
- ✓ **latitude**, **season** et **hour**, having an influence on Sun height and thus on energy received at the ground level

Received solar energy is:

- ✓ **unevenly** distributed
- ✓ of **variable** intensity
- ✓ **intermittent**

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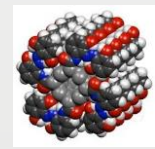
HOW TO STORE SOLAR ENERGY?

Various forms of solar energy storage:

- ✓ **Fuels** (solid, liquid or gas) = the most common forms of **fossil energies** (**coal, oil, gas**)
- ✓ **Electrochemical**: batteries/accumulators (to store electricity produced by **photovoltaics**)
- ✓ **Heat**: heat preservation in a material (for ex.: **solar power plant**)

How to convert solar energy into bond (chemical) energy in molecules?

=



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NATURE IS DOING IT (BUT QUITE SLOWLY)

Photosynthesis (plants, algae) started on Earth 2.5 Mds yrs ago.

Atmospheric O_2 is coming from it.

water + **carbon dioxyde** + light → **sugars** + **oxygen**

$H_2O + CO_2 +$ ☀ → **energy** + O_2

Taking inspiration from this = **artificial photosynthesis**

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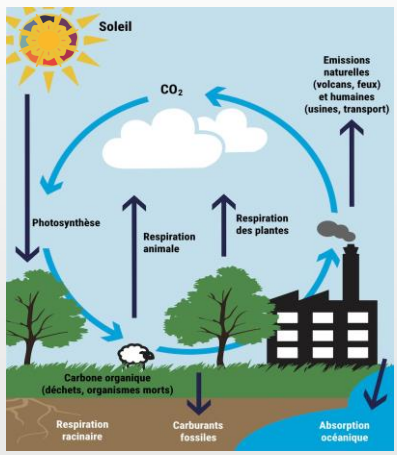
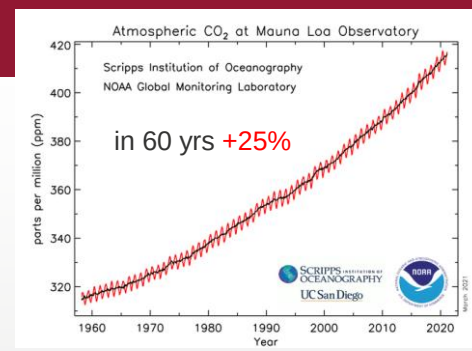
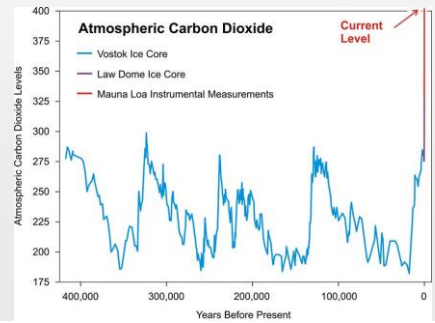
THE CO_2 CYCLE

CO_2 emissions (natural + anthropogenic) **overpass natural fixation capacities** => about **50%** of CO_2 emitted by fossile fuels uses is **not fixed**.

Major consequence: CO_2 is **accumulating in the atmosphère**







March 2021: 417 ppm (0.041%)

CO_2, AN UNDEREXPLOITED RAW MATERIAL

CO_2 is a **waste** (energy production, steel, cement, incineration, transportation…)

Current CO_2 price on the european market = around **25€ per ton**

(almost) all common fuels are **carbon-based** with E(C-C) = 350 kJ mol^{-1} :

- Wood (50% of C)
- Natural gas: 75% of **methane** (CH_4)
- **Ethanol** (« SP95-E10 ») : CH_3CH_2H
- Gasoline, kerosene, diesel… : **alcanes** C_nH_{2n+2}

What to do with this source of carbon, abundant, inexpensive but… problematic???

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INDUSTRIAL USES OF CO_2

Food and related (soft drinks, cooling) 8 Mt/an

Fertilizers (urea) 110 Mt/an

Technical uses (extinguishers, laser) 10 Mt/an

CO_2 captured

Methanol 24 Mt/an

Plastics/polymers 10 Mt/an

Fine chemicals (salicylic acid) 30 kt/an

Total utilization: around 160 Mt/yr
Human emissions: around 40 000 Mt/yr…

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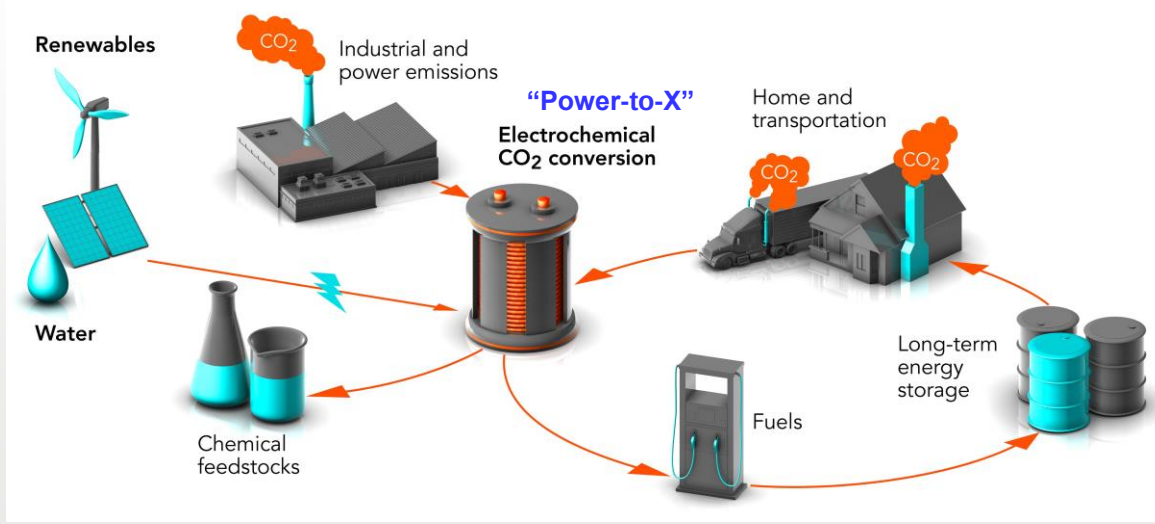
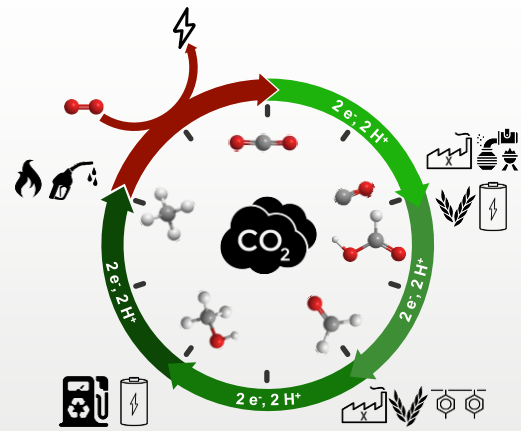
CO_2 CONVERSION BIG PICTURE



THE CO_2 CLOCK

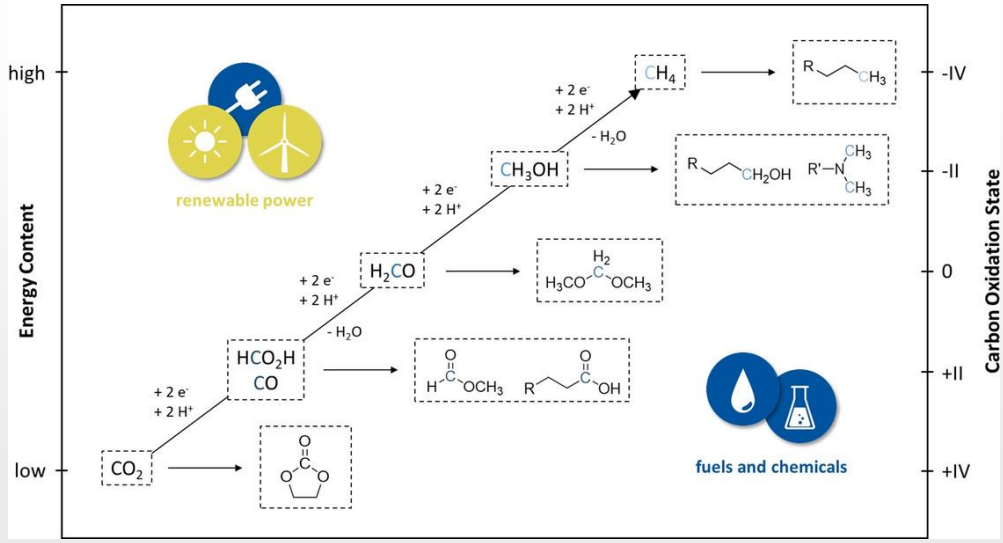
Reaction	energy (V)
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	-1.90
$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$	-0.61
$CO_2 + 4e^- + 4H^+ \rightarrow HCHO + H_2O$	-0.48
$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O$	-0.38
$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$	-0.24



CO_2 = ultimate oxidized state of carbon = a highly stable molecule.
By winding up the clock, reduced species can be obtained :

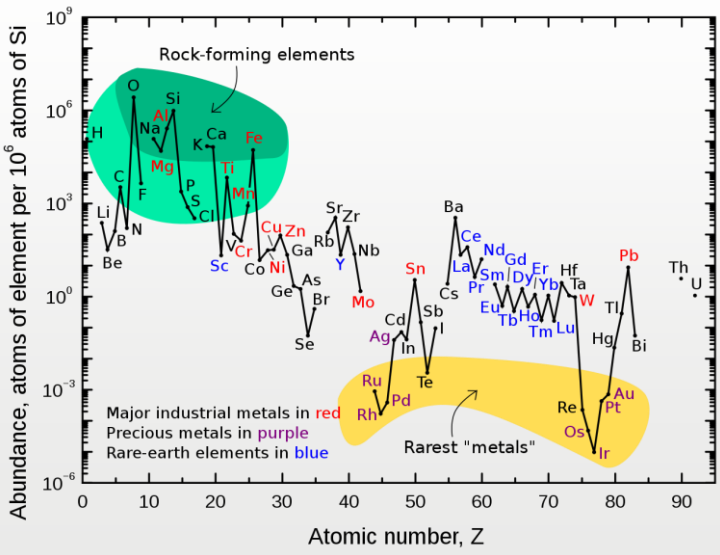
- ✓ Molecules for industry and fine chemistry (carbon monoxide, formaldehyde)…
- ✓ Fuels (methanol, methane)

FROM CO_2 TO ENERGY RICH C_1 COMPOUNDS



N. W. Kinzel, C. Werl, W. Leitner, *Angew. Chem. Int. Ed.* 2021, **60**, 2-6

WHICH METAL CENTER FOR THE CATALYST?



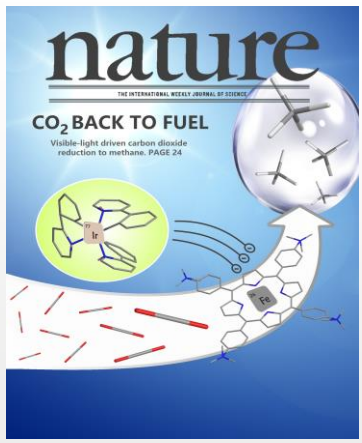
Desired criteria:
- ✓ abundant
- ✓ large and easy access
- ✓ non-toxic

Iron, **Cobalt**, **Nickel**, **Copper** are good candidates

PHOTOCHEMICAL CONVERSION INTO CH_4

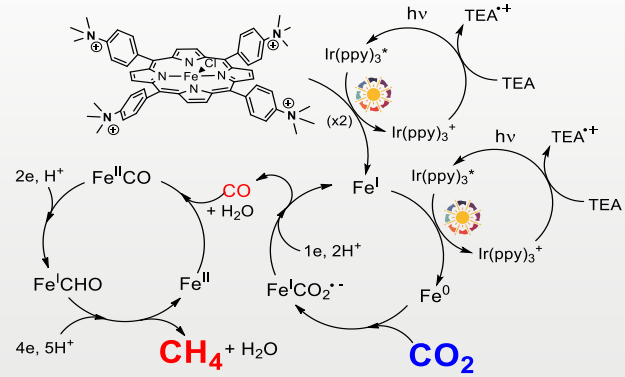
H. Rao

M. Kientz



Nature 548, 74, **2017**

CO_2 transformation into methane (CH_4) with solar light and an iron based catalyst



Renewable methane can be **directly used** in existing systems

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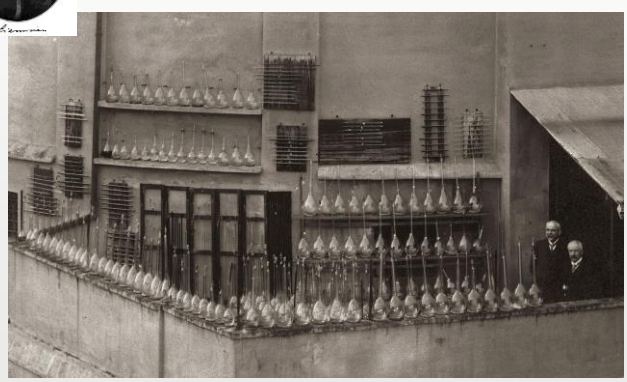
MARS MéthAne Renouvelable Solaire

GRDF GAZ RÉSEAU DISTRIBUTION FRANCE

"SOLAR FUELS", A CENTURY OLD IDEA

Giacomo Luigi Ciamician (1857-1922)
Italian chemist,
pioneer of the solar energy conversion



Bologna university around 1910

Université de Paris

SCIENCE 1912

THE PHOTOCHEMISTRY OF THE FUTURE

Modern civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

Even making allowances for the absorption of heat on the part of the atmosphere and for other circumstances, we see that the solar energy that reaches a small tropical country—say of the size of Latium—is equal annually to the energy produced by the entire amount of coal mined in the world! The desert of Sahara with its six million square kilometers receives daily solar energy equivalent to six billion tons of coal!

(...)

With convenient modifications could not this now actually be done on the tropical highlands? Yet the true solution consists in utilizing the radiations that pass through the entire atmosphere and reach the surface of the earth in large amounts. That a way of accomplishing this exists is proved by the plants themselves. By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes. The desert regions of the tropics, where the conditions of the soil and of the climate make it impossible to grow any ordinary crops, would be made to utilize the solar energy which they receive in so large a measure all the year, that the energy derived from them would be equal to that of billions of tons of coal.

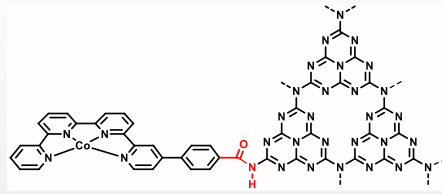
Besides this process, which would give new value to the waste products of combustion, several others are known, which are caused by ultraviolet radiations and which might eventually take place under the influence of ordinary radiations, provided suitable sensitizers were discovered.

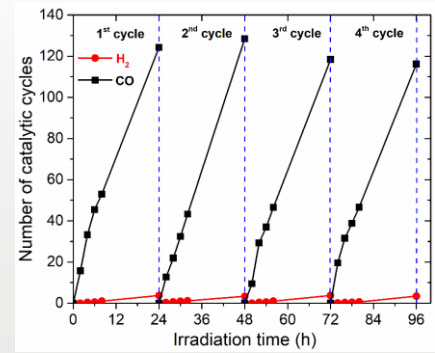
MOLECULE@MATERIAL HYBRID SYSTEMS

B. Ma

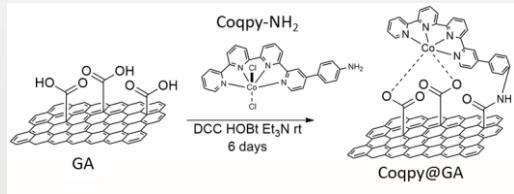
CO_2 reduction to CO under visible (solar) light
active catalyst = **Cobalt** quaterpyridine hydridized with….

Carbon nitride
(C_3N_4)





Graphene acid
(**GA**)



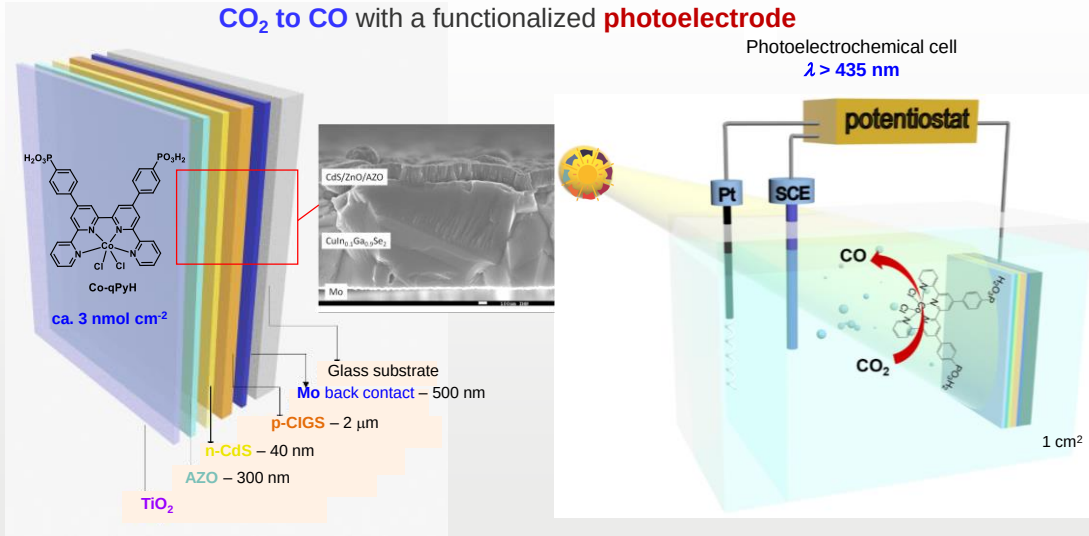
Angew. Chem. Int. Ed. 57, 7769, **2018**; *JACS* 140, 7437, **2018**; *JACS*, 142, 6188, **2020** + paper in revision

PHOTOELECTROCHEMICAL CELL (PEC)

E. Boutin

R. Wang

CO_2 to CO with a functionalized **photoelectrode**



Nature Commun. 11, 3499, **2020** + article in revision

ELECTROLYZER FOR "GREEN" CO PRODUCTION

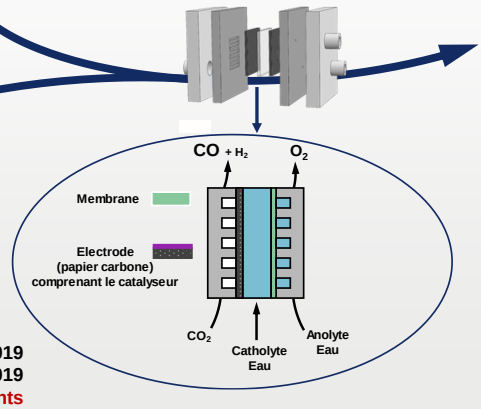
D. Joulié

Electricité propre

CO_2 + ⚡ = CO + ½ O_2

Monoxyde de carbone
+
Dioxygène

Dioxyde de carbone



Science 365, 367, **2019**
Nature Commun. 10, 3602, **2019**
+ 5 patents

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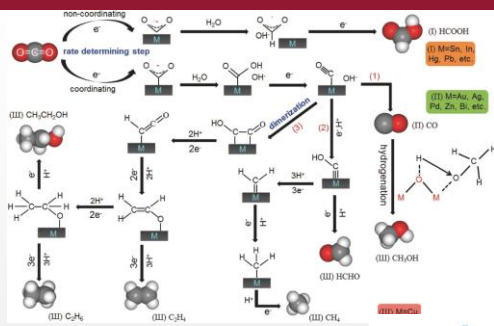
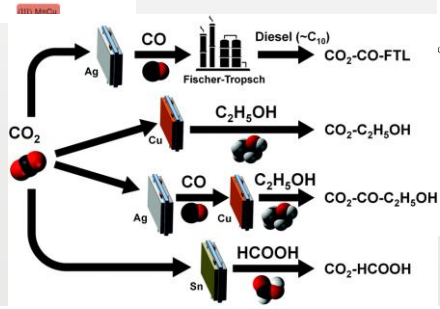
FROM CO_2 TO $C_1 \rightarrow C_N$ COMPOUNDS

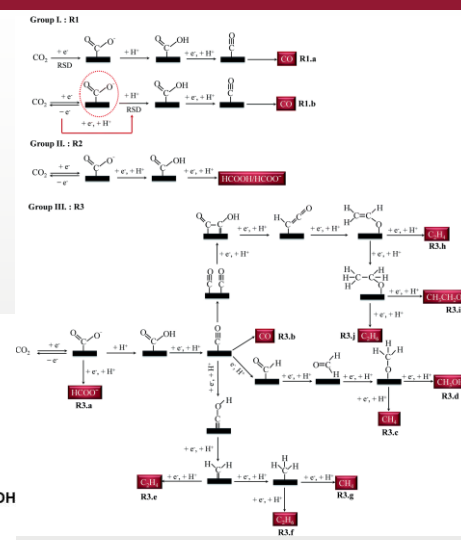


Adv. Sci., **2018**, 5, 1700275

more complex
and energy
rich molecules



Energy Environ. Sci., **2018**, 11, 1536-1551



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SOURCES

www.statistiques.developpement-durable.gouv.fr

+ AIEA, Conseil Mondial de l'Energie, GIEC
+ ENEDIS, RTE, GRDF, GRTgaz
+ scientific papers

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Thank you & questions welcomed