Carbon Dioxide
The Key Molecule of Sustainable Energy Development

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1. A Key molecule for the future

Carbon dioxide is a well-known molecule to our everyday life and is the vehicle for
1 photosynthesis energy storage and has been a key feedstock for the production of Fossil Oil, Coal, Natural Gas over the last millions of years on our earth… Incidentally, we can notice one of the behaviors of this molecule when having a glass of Champagne and observing the bubbles releasing it! (fig1a)

But do we suspect all the benefits we could get from re-engineering what nature has done so well for millions of year and how sustainable development could be impacted?

We will see indeed how Carbon dioxide can be key in three critical issues: Food ecosystems, greenhouse effects and energy storage.

1.1. The green house effect issue

For hundreds of millions of years, carbon dioxide has been a feedstock in solar energy stocking via photosynthesis. This natural process is at the root of vegetal life development as well as a key element of life cycles on our planet and particularly critical to human population development through agriculture (fig1 b, c, d).

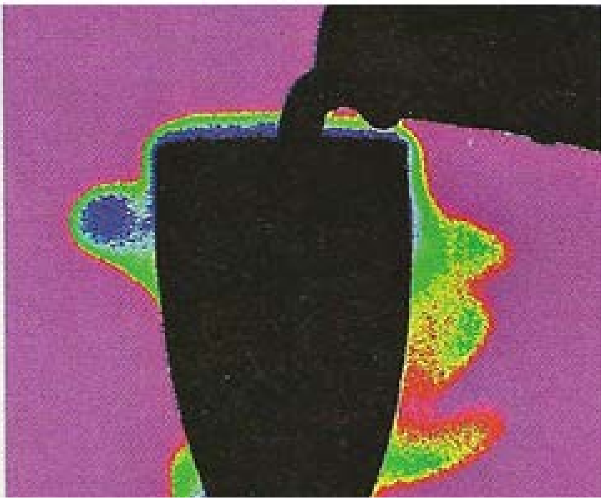

Fig 1 (a) Infrared thermography image of the gaseous CO_2 that flows out of champagne during the classic pouring method. (C&EN Chemical & Engineering News. P. 34. July 26, 2010)

This molecule also has a significant role in the climate of our planet through greenhouse effect and its concentration in the atmosphere may have influence on our climate and its evolution.

For all these reasons, Carbon dioxide is truly a key molecule in sustainable energy development and we may remember as well that it is a remarkable indicator of our consumption of fossil fuel energies.

Fig 1(b c d) - these slides point out that the key role of the carbon dioxide is to storage the sun energy through photosynthesis which is the key of life,giving us glucose ,starch and cellulose whichmeans food and vegetation for the biosphere

Let's explore the important stages of carbon cycles when the CO_2 molecule is transformed:

- During photosynthesis, the sun's action on chlorophyll (vegetal pigment) triggers the creation of glucose molecule out of Carbon dioxide (CO_2) and water (H_2O) (fig 2 a)

- On the other hand, we can also observe the combustion of carbon based materials such as wood or fossil fuels where oxygen triggers a reaction that will output CO_2, H_2O and energy
.

We have a natural solar energy storage process. The storage of energy and material can be further enhanced by polymerization of glucose leading to macromolecules of varied sizes. Some of which, like starch are well-known in food processing industry or like cellulose which is extensively used in paper industry(fig 2 b).
Throughout these examples, CO_2 appears indeed as a molecule to be used as a feedstock and not only considered as a waste: in other words, a molecule which is to be put to work through a chemical process.

Through Photosynthesis, Solar energy is stored in the form of sugar using CO_2 + H_2O in input. The Carbon backbone of the glucose molecules created in that process comes from CO_2.

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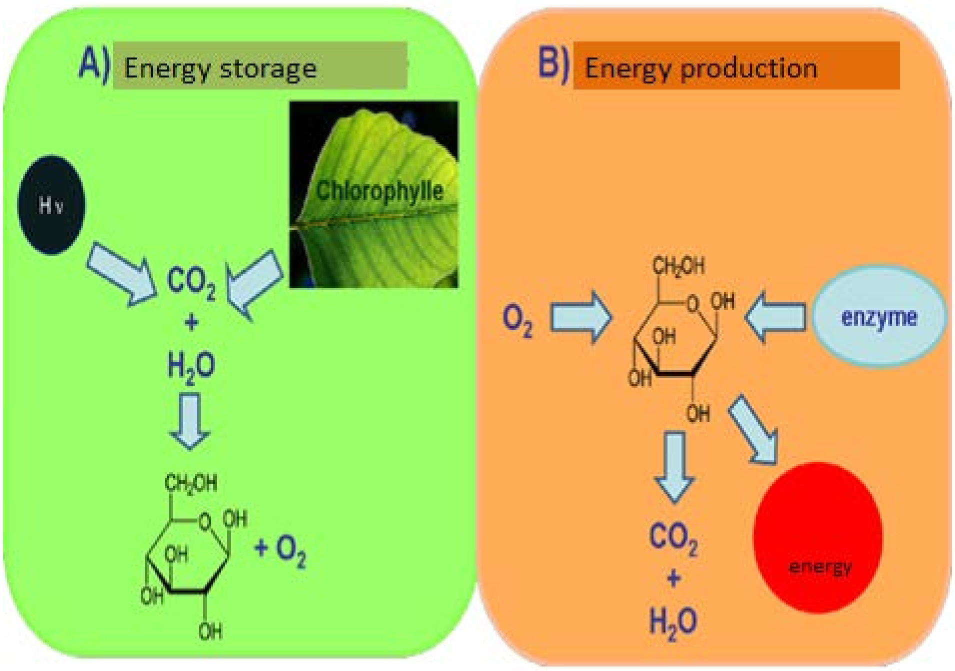

Figure 2

- A Step 1: Energy storage through photosynthesis (Mass balance : 6 CO_2 + 6 H_2O = $C_6H_{12}O_6$ (glucose) + $3O_2$) ;
- B Step 2: Energy production (Enthalpy of formation : -1273,3 KJ/mol).

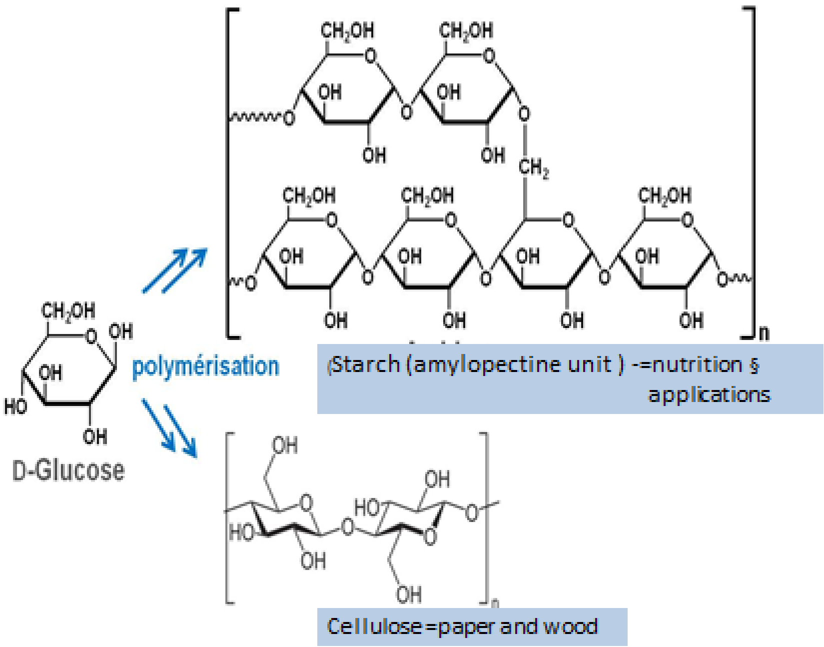

fig 3 – In nature, carbon dioxide is the raw material for glucose formation through photosynthesis and polymerization reactions gives starch,cellulose and others vegetal molecules. These molecules and material are one key step for many biosphere ecosystems and for technical activities such as paper,wood and textiles.

These reactions are part of the natural cycle of carbon (fig 4), in which CO_2 is transformed into plants and nutrient storage for animals.In the aquiferous (water bearing) part of this cycle, particularly in oceans, micro-seaweed are the starting point of the marine ecosystem.

Otherwise, cocolothophores (unicellular marine seaweeds) transform the CO_2 which is solved in calcium carbonate (CaCO3) in calcareous scale called coccolites. Their accumulation causes sediment deposits, such as chalk, to grow.

Lastly, in high depth, in absence of oxygen, bacteria transform CO_2 in methane (CH4) which turns into clusters which are part of rock deposits such as clathrate: The same clathrate from which we can extract shale gas by hydraulic fracking.

This well-known carbon cycle has been at work for millions of years. But over the last centuries, exchanges between vegetation, atmosphere and oceans has changed.It might partly be because of deforestation and maybe partly as well because of a more extensive usage of fossil combustibles.

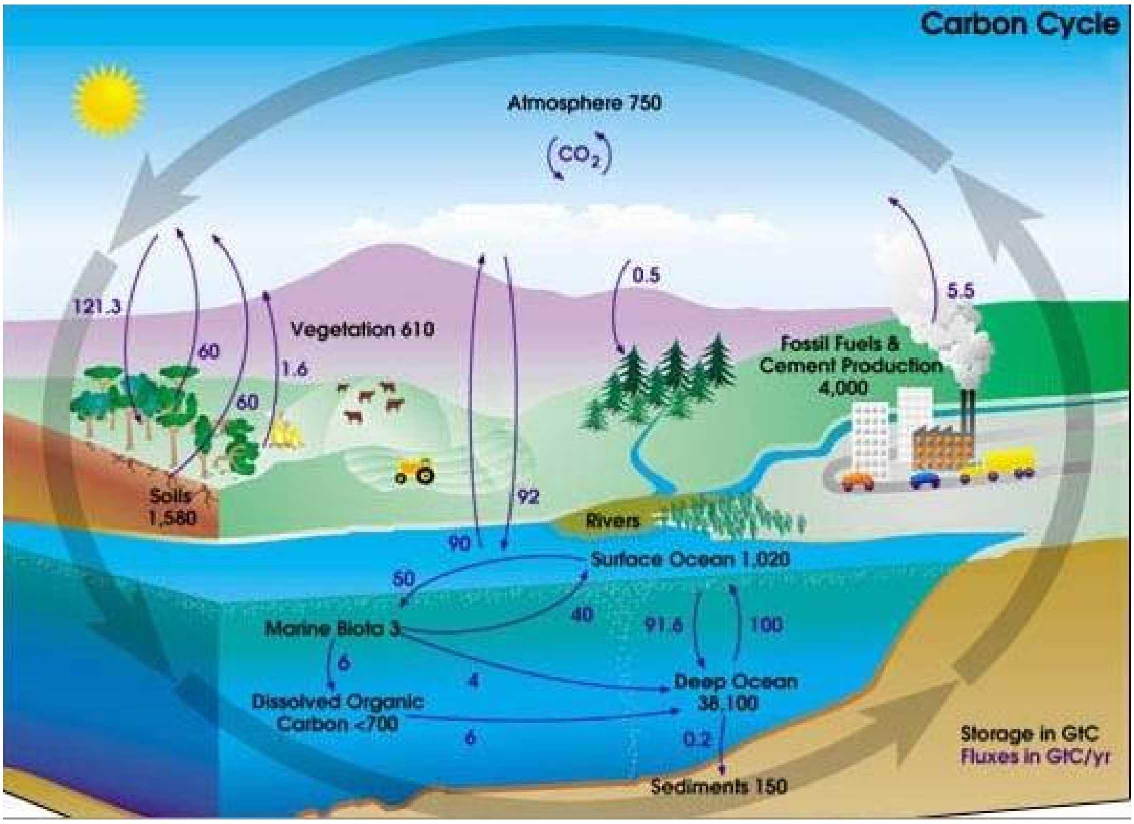

Fig 4– World carbon cycle

5 The carbon cycle is working since millions of years and explain the fossil carbon storage but deforestation and fossil combustion outputs and additional 8,47gigatons of carbon in theatmosphere each year.

(Source: ACS, 6 oct 2009)

We can observe a greater accumulation of CO_2 in the atmosphere and in the oceans (acidification of the oceans). (Fig 5). The increase of CO_2 concentration in the atmosphere may look relatively modest but it still represents an additional 35 Millions of tons of CO_2 each year.

What could be the consequences?

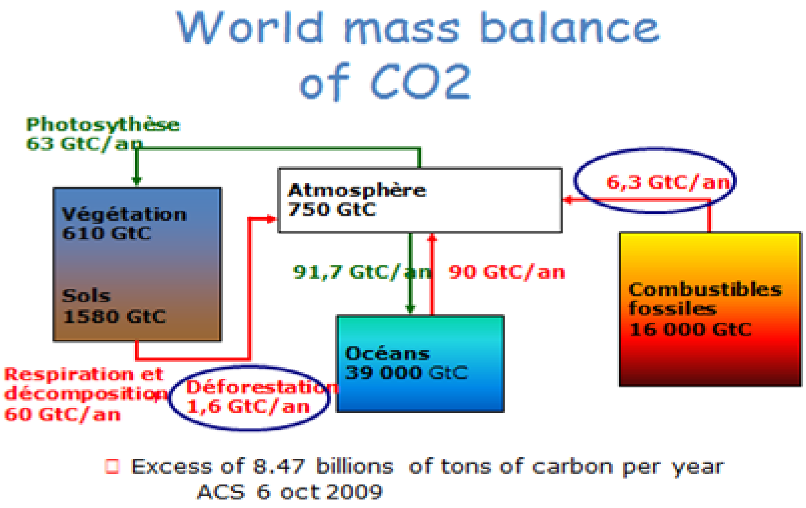

Exhibit 5 – world carbon mass balance each year (gigatons of carbon GtC).
The major mechanism is the large difference of kinetic between industrial production and vegetation enzyme reactions of storage

In studies completed by glaciologist Claude Lorius[1], it is shown that CO_2 atmospheric concentration increased from 280ppm one and a half century ago to 380ppm currently.These studies were conducted by using deep ice samples in glaciers.

One point regarding this analysis is to observe that CO_2 concentration in the atmosphere has been a good indicator of our consumption of carbon based fossil combustibles over the last 5 decades. One way of being creative could be by looking at CO_2 as a starting point and a feedstock to create or re-create energy storage and not as an output and a waste.

The European parliament has explored a political path in this regard that we will present later on.

One recurrent question today is: can we modify the role of carbon in our civilization?

There are tight relations between CO_2 outputs, consumption of our carbon based fossil fuels and energy usage in different sectors of our life. The increase in CO_2 output should lead us to think whether it is sustainable to keep going at the same pace and to explore in which areas we can « switch » energies, in which areas we will probably be bound to stick with carbon based fuels for a while and what we could do to curb a fast depletion and possibly initiate some repletion of our carbon based fuels.

1.2. Management of Carbon based energy sources

Figure 6 represents different energy sources and their interactions. On the right side, we have carbon based fuels and biomass which are used for transportation (aircrafts,vehicles, boats) and for heating which are CO_2 producers.On the left side, we have non carbon based

Claude Lorius was the chairman of the laboratory of glaciology and geophysics of environment in Grenoble (1983-1988) gold medal of CNRS electrical energy sources such asnuclear, wind power, solar energy, hydro and geothermal energies.

Solar energy is also the engine of agricultural production along with a key element: Water. Water depends on a thermic cycle going from the surface of oceans to the atmospherewith earth in between.

The evaporation of water and its condensation to our ecosystems. It can be stored in a natural or artificial manner and can be used as energy storage as well in dams (for hydraulic powerplants).

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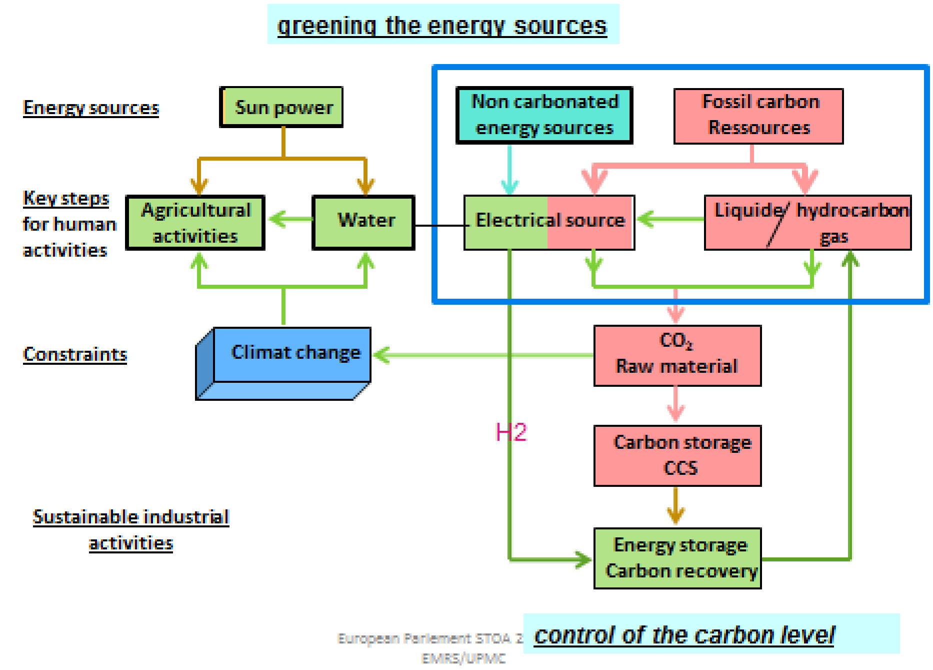

Figure 6: Energy Resources

Discussing the management of energy resources requires the have in mind a few key data regarding water, regarding the price and characteristics of the main known sources of energy.

1.2.1. Regarding water and energy production

The production of electrical energy requires a certain amount of water that varies according to techniques as shown in exhibit 1.This exhibit compares the necessary amount of water used for the production of one unit of energy (1 Megawatt-hour).

Let’s look at two interesting examples:

Gasturbines need 0.2 to 3 m3 per Megawatt-hour while in the case of biofuels (ethanol out of corn or biodiesel out of soybeans) 2000 m3 per megawatt-hour are required.

Table1— Water requirement for energy production: liter per MWh
Source-*Science*, 23 Oct. 2009, vol. 326.

Oil extraction	10 - 40
Oil refining	80 - 150
Coal integrated gaseification combined cycle	950
Natural gas combined cycle power plant	200 - 3 000
Nuclear plant closed loop cooling	950
Geothermal powerplantin close loop tower	1 900 - 4 200
Enhanced oil recovery (EOR)	7 600
Nuclear power plant open loop cooling	94 000 - 277 000
Ethanol from Corn (irrigation volume)	2 270 000 - 3 670 000
Soybean biodiesel (irrigation volume)	13 900 000 - 27 900 000

1.2.2. The Price of Energy (**Science, 12june 2009, vol 324, p. 1389)-(Energy Environ.Science, 2010, vol3, p.28)**

For different kind of resources, table 2displays a comparison in USD per GigaJoule.
We can observe that Oil price which is currently between 105$ and 125$ per barrel implies an energy price between $15 and $20/GJ.
On the other hand, Natural Gas in the US has tumbled down from $4/GJ to $2.0/Gj in 2012 following massive supply from shale gas wells (500 000 Shale gas wells have now been opened in the US)
Coal is around $2/GJ ($1.4/GJ for Illinois Coal)
Lastly biomass comes around $3.8/GJ and wood at $11/GJ

Tableau 2 - **Price of Energy (in $/gigajoule).**

Cost of raw material	price of energy
Oil :$60per barrel	$10 (2009), $12.5 (Sep 2010)
Oil : $85 per barrel	14
Oil : $90~$107 per barrel*	$15-$17 (March 2012, West Texas Intermediate)
Oil :$105-$125 $ per barrel*	$17-$20 (March 2012, Brent)
Nat Gaz (US) Shale gas	$4 (août 2010) $1.99 (april 2012)
Coal (US, average $60/T ; $37/T for Illinois)	$3,2 - $3,7 (2012) ($1.44 for Illinois)
Coal (Europe, 2010 average : €75 ~ 100 €/T)	~$7.00
US dry biomass feed stock (from cornstover)	$3,8 (for productions >1 Mio Tons)
Wood pellets (USA, $200 /T in 2009)	$11
Wood pellets (USA, $400 /T in 2013)	$22
CO_2 ETS	$8~11 $ per ton (Jan 2012)

1.2.3. Worldwide energy needs

By extrapolating data from table 2 up to 2050, the electrical energy needs have been estimated assuming a population of 9 bios (Table3).
With the energy price and availability data mentioned earlier in mind, two main energy sources will emerge ascritical: Coal and Nat gas. Their production should be multiplied 2.5 times to 3 times for Nat Gas.
On the other hand, renewable energies such as solar/wind/geothermal/hydro should also step up significantly in output.

These data allow us to catch a glimpse of what global CO_2 output will be, coming mostly from carbon based fossil fuels: Coal/Shale Gas/ Oil.

How to tackle this issue while handling the sporadic availability of renewable energies such as wind power and solar energy?

Table 3 - Extrapolation of the world electricity production (billions of MW.h).

9

	2020	2050
Coal	6,1	16,7
Petroleum	0,694	0
Natural gas	5,6	13,9
Renewableenergy	1,4	5,6
Nuclear Power	2,2	2,8
Waste	0,694	1,1
Cogeneration	2,8	5,6
Total	19,4	45,6

Mapping renewable energies in the changing needs of energy should consider several characteristics: their variability, their intermittency and their density. For instance, it is interesting to notice that wind-power doesn’t produce energy on demand but only when there is wind and this is not bound to match peak demand. As a matter of fact, it almost never does. In the case of solar power, although we know cycles better, we have similar issues as demand variation does not match supply cycle.

Yet, our civilization is used to having energy « on demand » and used to be able to switch on light, coolers, and heaters when needed. This apparently « normal and natural » demand impliesextremely tight energy production requirements in terms of organization and speed of response.

In this context, how do we develop renewable energies and try and adaptsometechnologies to our needs and some needs to new technologies?

1.3. What challenges are we up against in the field of future energy resources and how will the current energy sources evolve?

One major challenge today is in the field of energy storage of renewable energies: how to « store for later » these new sources energy which are producing at times « uncorrelated » with our demand.

In this field (energy storage), several tools are starting to appear andon the way to dramatic improvements.

- For instance, Lithium-ion batteries which are the top of the line in battery technology have an energy density of approximately 250 Watts-Hour/Kilo. In other words, 60Kg of battery can store 15 KW-Hour. In comparison, a 60Kg fuel tank generates 660 KW-Hour, which is 44 times more!!
- Another highly relevant idea was proposed by 1994 Nobel prize Pr. Georges Olah: Using CO_2 as a feedstock + energy (compression) + Hydrogen (H_2) to synthesis fuel. In this case CH_4 (Methane) or CH_3OH Methanol. These techniques are a particular case of a Fischer-Tropsch process where CO or CO_2 + H_2 is combined using Cobalt or other metallic based catalyst (mainly iron) to output hydrocarbons ranging from CH_4 to longer hydrocarbon molecules such as olefins and paraffins.

Let's explore the current state of the art in this area with the idea of potential application to renewable energy development

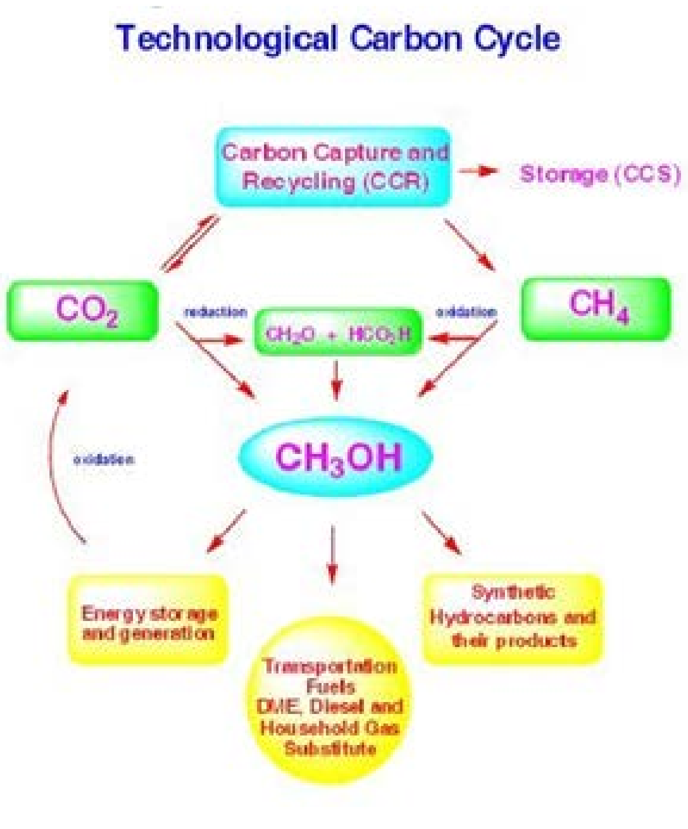

Figure 7
Proposals for carbon dioxide valorization from George Olah Nobel, Prize of Chemistry 1994

2. CO_2 challenges

In an endeavor to manage the future of energy supply in Europe, The European commission have tried to develop a market for carbonemission taxes (ETS) in order to « manage » the emissions in the form of a tradable quota. It started in 2005 with the objective of « capping » CO_2 emissions via a carbon tax imposed on these companies going over their freequotas.
A second important parliament has undertaken the following steps as soon as November 2008: European set plan: 20% reduction in CO_2 emission, 20% of energy output from renewable energies, 20% of improvement in energy technologies.

Meanwhile, some of the most ambitious strategies so far have focused on improving the energetic yield in fossil fuel based operations. Currently this yield averages around 38% over fossil fuels and reaches only 10% in the case of coal for instance. Indeed, in between the primary source and the operation, a lot of energy loss (leakage, inefficiencies) gets in the way. First of all,energy loss occurs through the number of different steps which are necessary to get from the raw material to the finished product. Also each of these steps is not necessarily optimized:For instance, coal is currently as expensive to transport as it is to extract. There are indeed considerable room for improvement which will require researchs and investments in newer technologies.

11 Today, research has started to look toward that key molecule of Carbon dioxide as a key element; to retrieve out of our carbon based fuel operation, as an element to capture, to store and to reuse as a feedstock in several different ways.

What are the different routes that have been explored in this field and how far did research go and what didit delivered so far?

2.1. CO_2 Capture & Storage

These processes abbreviated under the acronym « CCS » for « carbon capture and storage » aim at extracting CO_2 from industrial exhaust gases, mainly from coal power plant or cementry or steel making in blast furnace etc. Most techniques used to extract CO_2 from these gas mixtures will use ammonia based « washing » processes where other chemical components such as nitrogen oxide (NOx), mercury, sulfur oxides will be put aside. Carbon dioxide will then be absorbed also inammonia refrigeratedscrubbers then the ammonia-CO_2 liquid will be heated again, ammonia will be recycled and the CO_2 captured. (fig.8)

This process was tested in United States on a 300 Mega-watt Coal power plant by Alstom. In France,The French Environment and Energy Development Agency (ADEME : Agence de l’environnement et de la maitrise de l’energie) is sponsoring a carbon capture development program on a coal power plant in Le Havre and the entire plan also comprises a CO_2 storage project in deep ground.

Otherwise, the European commision launched a 1 Billion euro program per unit on ten 1000 Megawatt Coal power plants; the goal is to capture 5 Bios Tons of CO_2 per year at a cost of 200 Euros/Ton. The 10 year goal is to go down to 25 Euros per ton with techniques using ammonia, or amines, Zeolithes or even cryogenic capture.
China for instance who depends heavily on Coal power plants is also developing such units some of them in joint-venture with Alsthom.

It is important to mention that the CO_2 captured by such processes reaches a purity of 99.9% which is critical to allow its proper compression and transport.

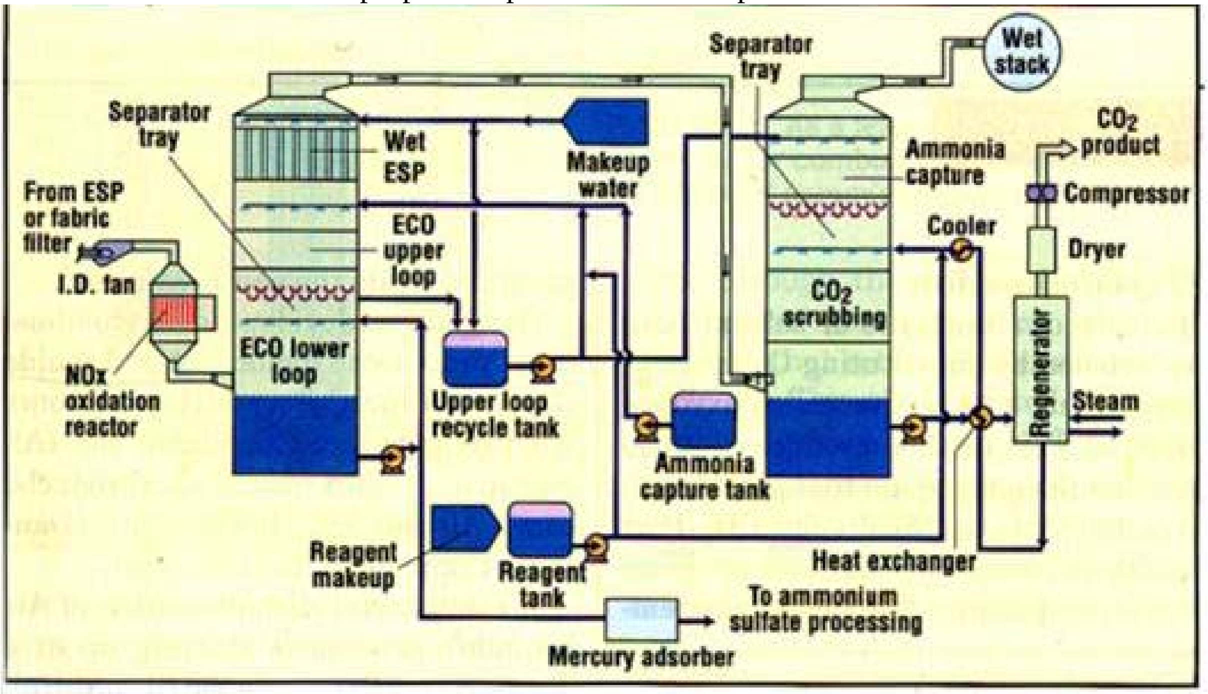

figure8 – CO_2 capture process of coal combustion exhaust gases by ammonia scrubber and electrocatalysis of nitrous oxide gas (« electrocatalyticoxidation », ECO).
Source:Chemical Engineering, Dec. 2003, p. 7. Power span Conf. Portsmouth, NH, USA.

2.2 Put CO_2 to work as a solvent

CO_2 is an efficient solvent which can be turned into a liquid at 70 Bar pressure and 30°C. It can be used in the extraction of oil and is name is enhanced oil recovery (EOR): one Ton of carbon dioxide allows extracting another 1.5 Ton of Oil. The Abu Dhabi International Conference on oil development has gathered the main players in the industry around a key question: increase the yield of current wells by horizontal drilling and injection of liquid CO_2 to « push out » the oil.

Otherwise, in the USA, the*Wall Street Journal* from Jan 7th, 2012 has published an article explaining that an increase in American oil production is expected by the end of 2013

Moreover, the Chinese group Shenshua has undertaken a Capture and Storage project of 3.6 Mios tons of CO_2/year dedicated to improve the yield of their oil extraction operation in Inner Mongolia.

2.3 Put CO_2 to work as a feedstock in an energy storage process: Toward electrical networks control and fuel supply for transportation.

To secure a sustainable energy development plan, it is critical to think of the integration of these « new » energies into our electrical networks and plan their addition to our « smart grids ». As timing of use of discontinuous electrical power is critical to the smart grid organization and timing is not an option « to be chosen » in the main sources of renewable energies such as Solar/wind and geothermal, it is therefore necessary to create « buffers » in the form of energy storage. Using renewable energies at a time when demand is not there can be one method to put CO_2 to work as a feedstock to recreate hydrocarbons via methane or Fisher-Tropsch processes. The energy storage is then achieved in the form of hydrocarbon synthesis.

In this field, several strategies are to be envisioned (some of them are already in use), they are shown in fig 9:

On one side we have the CO_2 producers : Coal, Nat Gas, Fuel power plants, waste treatment and burning factories, cement factories, fuel oil factories and on the other side we have non carbon based energy sources (Solar, wind , nuclear, geothermal power plants). The latter is in development in Europe but the production is non-constant and sporadic unlike the former
13 which can produce energy on demand but also outputs CO_2.
It is therefore possible to put CO_2 to use as a feedstock in several ways:

-By transforming CO_2 in Methane at non-peak hours to regulate electricity production. (Paragraph 2.3.1.);
- By transforming CO_2 in Methanol which is a highly useful intermediary product in many chemical industrial processes including the synthesis or hydrocarbon. (Paragraph 2.3.2.) ;
- Bygasificationof coal in order to improve the efficiency of its extraction by using plasma for instance (paragraph 2.3.3.);
- By putting CO_2 to react with Hydrogen on metallic catalysts: these are Fischer-Tropsch type processes (originally $CO + H_2$). The outputs range from Methane or Methanol to the longest paraffin with most of the types of hydrocarbons « in between ». (Paragraph 2.3.4.) ;
- By using CO_2 in the farming of micro-algae that can synthetize various molecules, some of which being hydrocarbon fuels. (Paragraph 2.3.5.) ;

- By using it as one of the feedstock necessary to synthetize polymers (Paragraphs2.3.6.and 2.3.7))

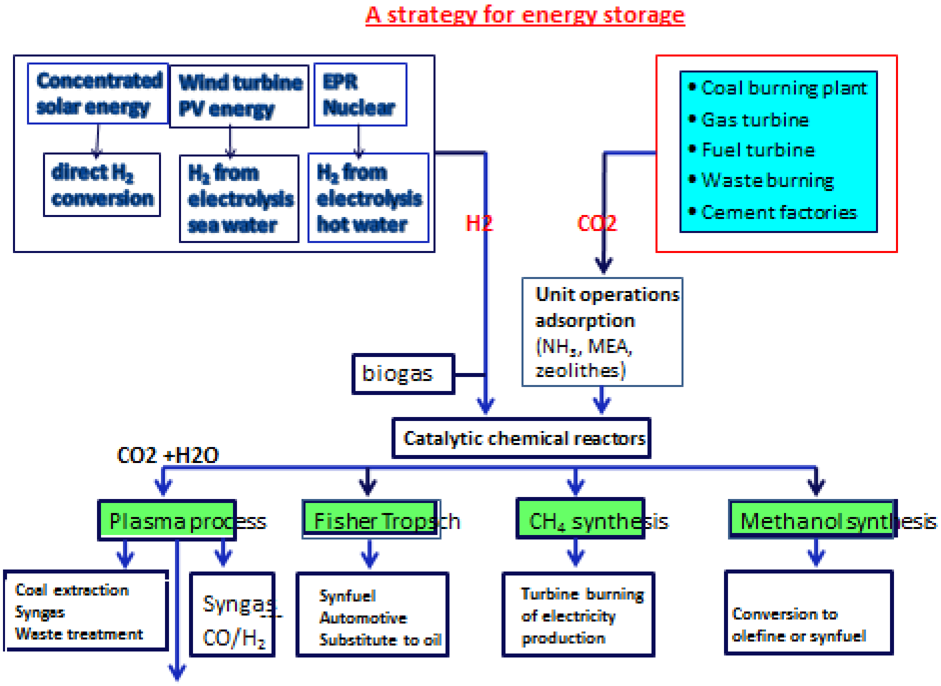

Figure 9 different processes of carbon dioxide valorization
Source: E-MRS FALL MEETING, Varsow 13-15 Sept. 2010 J. Amouroux, Symposium A

The figure 10 give an over view about the main ways to transform carbon dioxide in new hydrocarbons and chemical products such as methanol (CH_3OH), dimethyl carbonate (DMC), dimethyl ether (DME), formic acid (HCOOH) for textile dyeing, synfuel for transportation or Methane for network regulation.

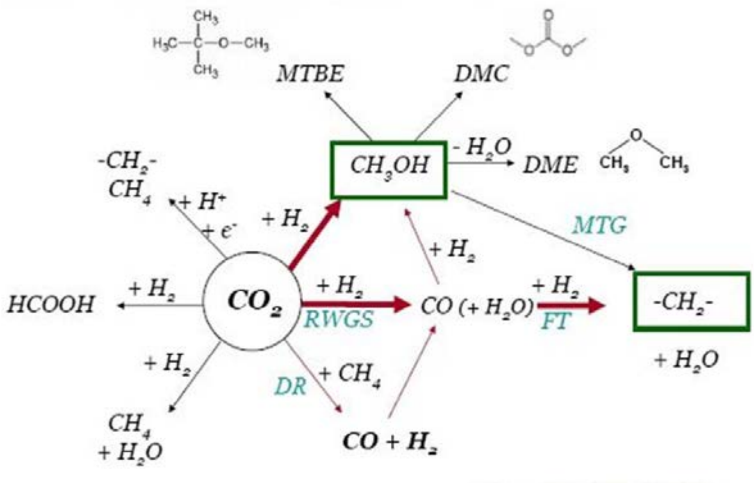

Figure 10 – chemical pathways from CO2 to liquids
BMBF-Max Planck Institute-Siemens seminar 22/09/2009 Warsaw Sept 2010
DME = diméthyléther, MTBE = méthyltributyléther, DMC = diméthylcarbonate; HCOOH =formic.acid

2.3.1. Transform CO_2 into Methane

Germany decided to launch in 2012 a 2 Bios Euros Research and Development program on electrical energy control and renewable energies. Part of the program includes the use of Methane synthesis from CO_2 to help and control gaps between sporadic production and demand. CO_2 can therefore be considered here as a true feedstock.

The mechanism illustrated in figure (11) looks straight forward: Out of sea water and a renewable energy such as wind or solar, H_2 is generated by electrolysis. Then by reaction between CO_2 and H_2 (with metallic catalyst (Ni) and high pressure), Methane can be synthetized. In return, it will be burned to release energy on the grid during peak hours. One KW-Hour of energy stored in off-peak hour allows generating 0.5 KW-Hour at peak hours when electricity is 10 times the cost which gives a positive financial output to the process.

One test project has been developed in Japan by Professor K. Hashimoto from Sendai Technology Institute (Exhibit 12). In this operation, CO_2 is transformed into Methane by using electrolysis using sea water and metallic catalysts (catalysts are based of Zircone-Samarium ceramic with a layer of amorphous Nickel as the catalyst active sites).

This operation has been transferred in Thailand as part of a joint venture between Hitachi Zosen Corp, Daiki Ataka Engineering Corp and PTTEP which is a Thailand national petroleum corporation in order to develop further a solar energy based operation that will synthetize methane out of CO_2, from sea water and solar electrical energy.

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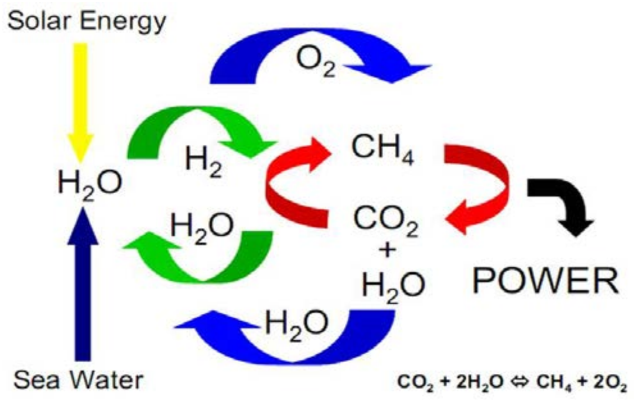

Figure 11 - Conversion of CO_2 into methane CH_4.
Ref : Martin E. Carrera Manager Biotechnology BP, E-MRS Paris 5/02/2008

Figure 12 - Emeritus Professor K. Hashimoto from Tohoku University (Institute for Materials Research, Sendai Japan) has developed for the last 20 years a pilot to realize the first process of methane synthesis from CO_2 by using sea water electrolysis with specific electrodes with Nickel based catalysts.
A) Lab size electrolyzer used to generate hydrogen
B) Bi-level reactors with heat exchanger in between the two levels in order to transform CO_2 into methane.

2.3.2. Transforming CO_2 into Methanol

Captured CO_2 can also be transformed into methanol and become a new feedstock for chemical engineering through that route. Methanol has the advantage of being a liquid at normal conditions of pressures and temperature therefore, its storage is not 22.4 Liters per mole but 0.32l per mole and it opens the way for diverse industrial chemical applications ranging from olefin synthesis (such as polyethylene, polypropylene) to protein extraction in micro-algae farming with other various applications such as improving the octane of traditional gasoline.

Methanol is synthetized as follow: $CO_2+H_2 \rightarrow CH_3OH+H_2O$, at 300°C under 70 bars in a reactor with a metallic catalyst (Based of Copper and Zinc on an alumina based ceramic).The ceramic is particularly adapted to this highly exothermic reaction ($Cu/ZnO/Al_2O_3$).An industrial size operation has been developed by Mitsui chemicals (Chemical week, May 3rd, 2010) and it currently produces 1 Mios Tons of Methanol per year.

Transforming methanol in polymers is also a route that has been explored: The Chinese Dalian University has realized an industrial size reactor using a fluidized bed technique to transform methanol into Propylen and Ethylen and it outputs 600,000 Mios Tons per year.
(Chemical Engineering Jan 2009 p 13) (Fig 13)

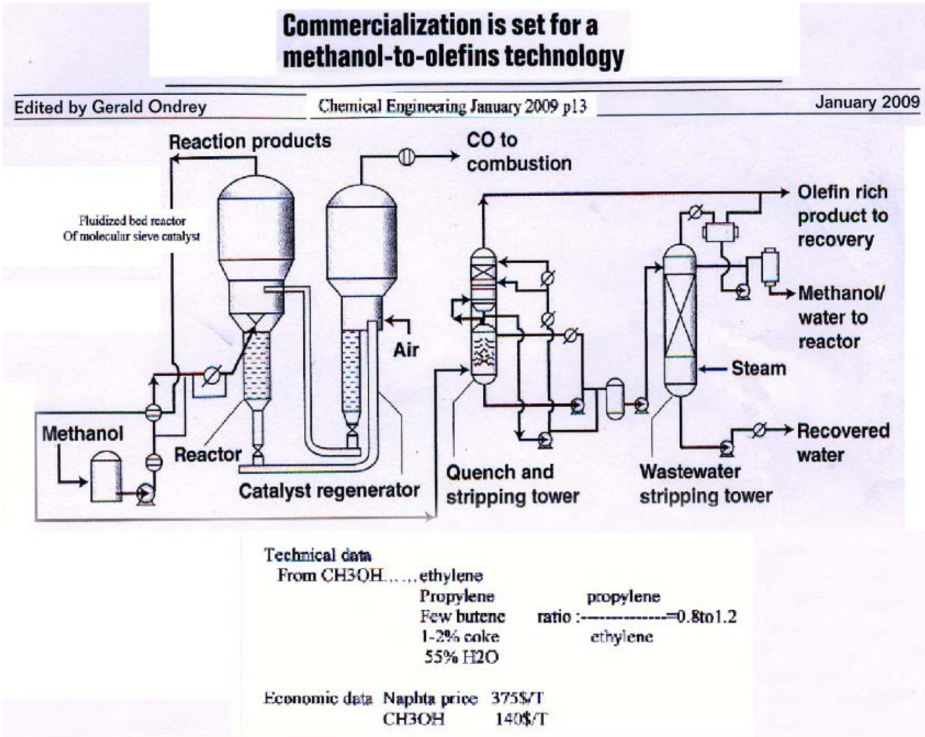

Figure 13: methanol to olefins technology ,this technic uses a catalysis fluidized bed reactor (molecular sieve) which transforms CH3OH to ethylen and propylen, at the out side a stripping tower separate olefins to water and methanol ,while the last column permit the recycling of methanol and the elimination of the water*(ref Dalian University China)*

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2.3.3. Using CO_2 to transform Coal in Syngas

As Coal transport is relatively high and not so flexible- As expensive as the extraction itself for a typical transport of a 1000 miles or so- It make sense to explore the route of transforming Coal into syngas on the spot and then use pipes to convey the syngas up to electrical power plants or to be supplied to chemical operations where itwill be converted to hydrocarbon fuels by a Fischer-Tropsch process.

Transforming Coal in Syngas is an endothermic gasification. It can be achieved using CO2 in a reaction called « Boudouard »reaction

$$C_{solid} + CO_{2\ gas} \rightarrow CO + CO_{adsorbed}$$
$$CO_{adsorbed} \rightarrow CO_{gas}$$

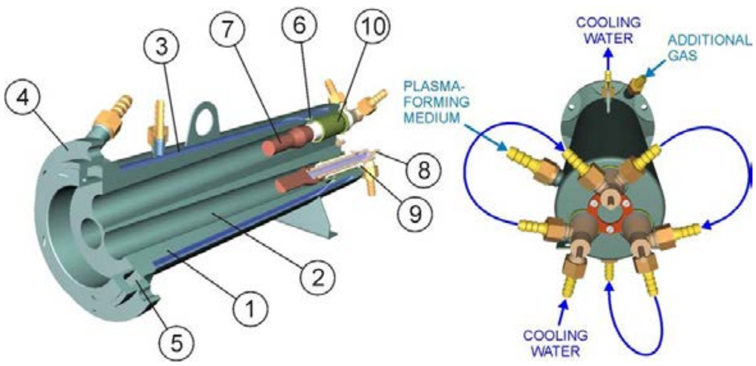
This endothermic reaction require energy ($\Delta_r H_f$=172, 3KJ.mol^{-1}) but also require the coal to be grinded in order to be used in reactors with fluidized beds at 1.5 MP.

In the framework of a European Commission program, a Polish team has developed a gasification reactor using a mix CO_2+O_2 on a COAL fluidized bed.The next step in the project will consist in developing an on-site operation using horizontal drilling techniques on coal layers in order to realize gasification directly at the source. This method requires producing oxygen beforehand which can be done by air distillation.

In order to avoid this step, another technique has been developed by a Russian team who intend to use electrical energy through a plasma torch using pure CO_2. (Figure 14). These plasma torches have a power ranging from 1 to 10 Megawatts and allow the cracking of CO_2 into CO + O and by reaction on a fixed coal bed. It gives 2 CO molecules which can be used for energy storage.

An experimental unit has been built by Professor P.Rutberg from the Saint Petersburg Institute for Electric Power and Electrophysics (figure 15). It comes with several technical improvements in the electrodes which save the erosion by the atomicoxygen produced by the plasma so that the life-time of a unit was extended up to 2000 hours.

This unit produces syngas either on a coal bed or on reacting materials coming from disposable municipal waste. This syngas can be used either to synthetize hydrocarbon fuels or to produce electricity.This flexibility allows matching the timing of demand from end-consumers.
This technology (figure 16) has been transferred to Japan in the form of two industrial operations managed by Hitachi Metals LTden.



1-CASE
2- DISCHARGE CHANEL
3- COOLING JACKET
4- FLANGE
5- ADDITIONAL AIR DISTRIBUTOR
6- WORKING MEDIUM DISTRIBUTOR
7- ELECTRODE
8- ELECTRODE HOLDER
9- CERAMIC INSULATOR
10- SEALING BUSHING

a) Air plasma　　　　b) CO_2 plasma

Figure 14-.THREE-PHASE PLASMA TORCHES for coal gaseification
PLASMA-FORMING MEDIUM: AIRPOWER: up to40 kWVOLTAGE 6-10 kV
CO_2 POWER: up to 50 kW

Figure 15–Experimental plasma process for coal and waste gazeification (Russia)
’Institute for Electric Power and Electrophysics of Saint-Petersburg (Professor Phillip. Rutberg (RAS))

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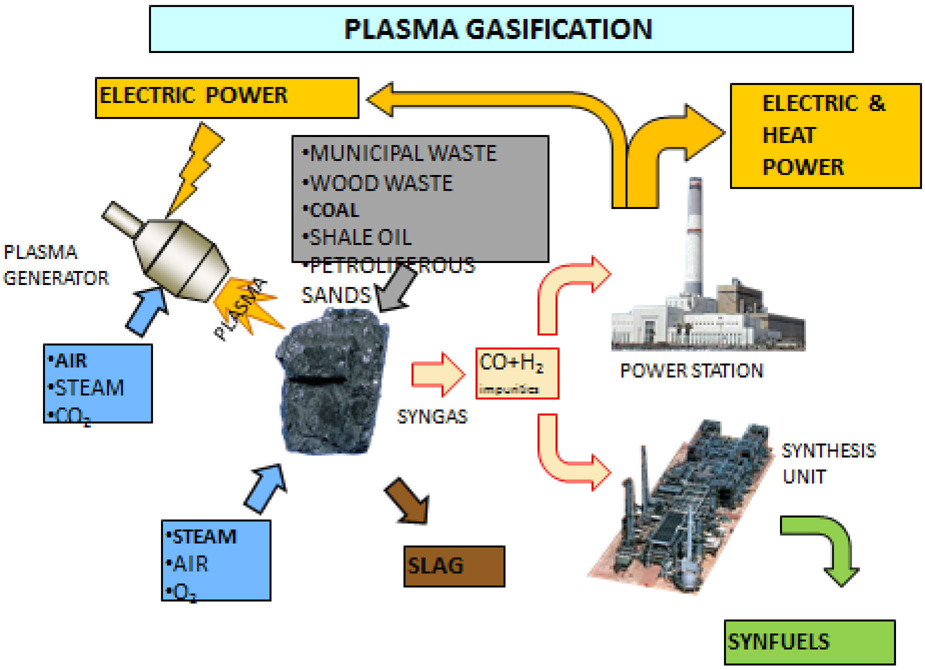

Figure 16–gaseification process by carbon dioxide three phase plasma torch. (Phillip Rutberg RAS)

2.3.4. Transforming CO_2 into Hydrocarbon fuels (Fischer-Tropsch process)

Transforming coal in syngas CO + H_2 then into Hydrocarbon fuels is called the Fischer-Tropsch process. It has been invented and developed by two German Chemists in the 1920s. Then this process was used by South Africa during their embargo in order to have use of liquid fuels. More recent studies have been realized by Dr. D Hildebrand in South Africa and made it possible to engineer a process to directly convert a mix CO_2+H_2 into Liquid Fuels. This process was patented in 2007 and several experimental units have been built to produce diesel fuel. (Figure 17).

China is working as well in this area in Inner Mongolia: The Senshuagroup has started a program named « Erdos » whose goal is the production of 1 Mios Tons/ Year of Diesel using that technique.

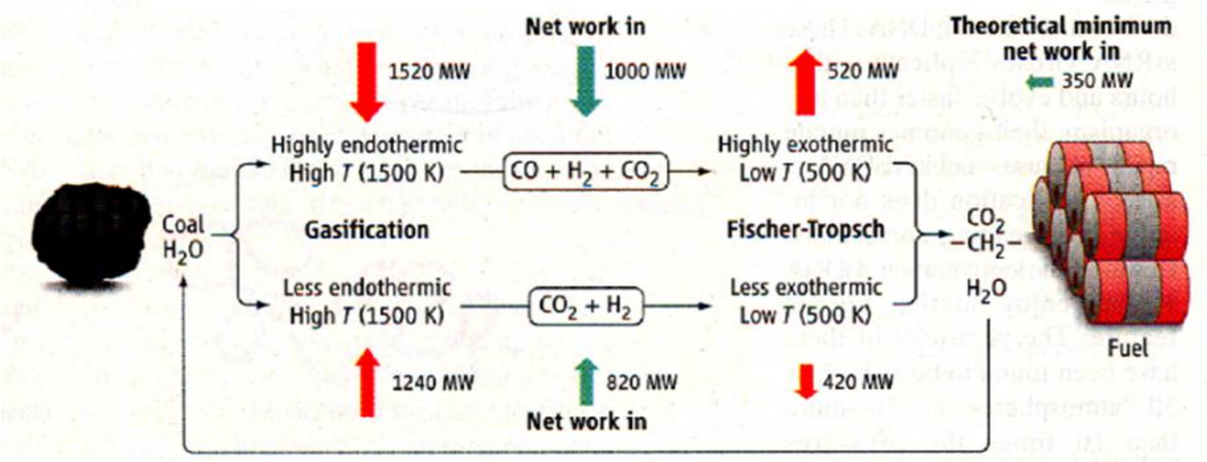

Figure 17– A new Fischer-Tropsch process: coal to fuel *via* the gas mixture CO_2 + H2.
(Brevet: D. Hildebrandt, D. Glasser, B. Hausberger, International Patent application WO/2007/122498) (Science, 2009, *323*, p. 1680).

2.3.5. Putting CO_2 to work for the production of Micro-Algae

This new process consists in using CO_2 to give a boost to the photosynthesis of Micro-Algae order to achieve better yield in the production of proteins and lipids coming from these Algae.
This technique finds application in cosmetics, in food preservatives and in biofuel production. Several research centers such as the French INRIA, University of Montpellier, University Pierre et Marie Curie have been involved in developing these techniques alongside with several industrial groups. Also, in Spain the Almeria center has been working thoroughly in that field over the last five years.
In Montpellier, an « ALGOTHEQUE » (Algae library) has been created and has become a repository of thousands of different algae species which are classified in a database and can be searched for according to their properties and the characteristics of the proteins or lipids that they can help synthetize.

Figure 18 shows a diagram of a diesel production operation out of micro-algae farming in an Australian facility.

By comparison with other biomass processes:
Rapeseed Oil outputs 1g/m2/day
Cane Sugar outputs 10g/m2/day

MicroAlgae ouputs 50g/m2/day

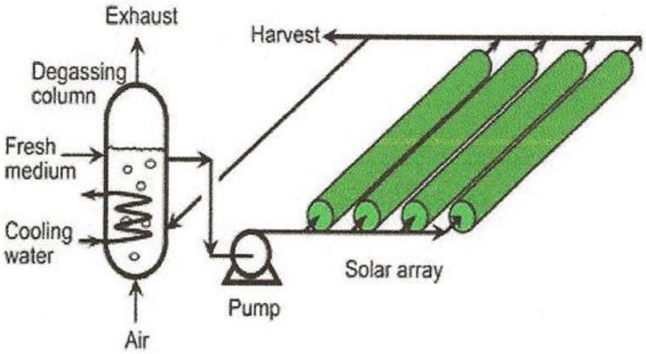

Fig 18 – Tubular Bioreactor of 1 000 liters (Murdoch Université - (Australia) for biodiesel production from micro-algae (1 kg of microalgea get1,8 kg of CO_2).

2.3.6. CO_2 as a new feedstock for chemical engineering

Out of a highly purified Carbon dioxide, high added value chemicals can be synthetized for the benefit of a wide variety of sectors of the chemical industry. Some of these applications are shown in figure 18 where we have CO_2 as a base product of petrochemical industry. For example urea (NH_2-CO-NH_2) production one of the most classic fertilizant is around 70.000T/Y

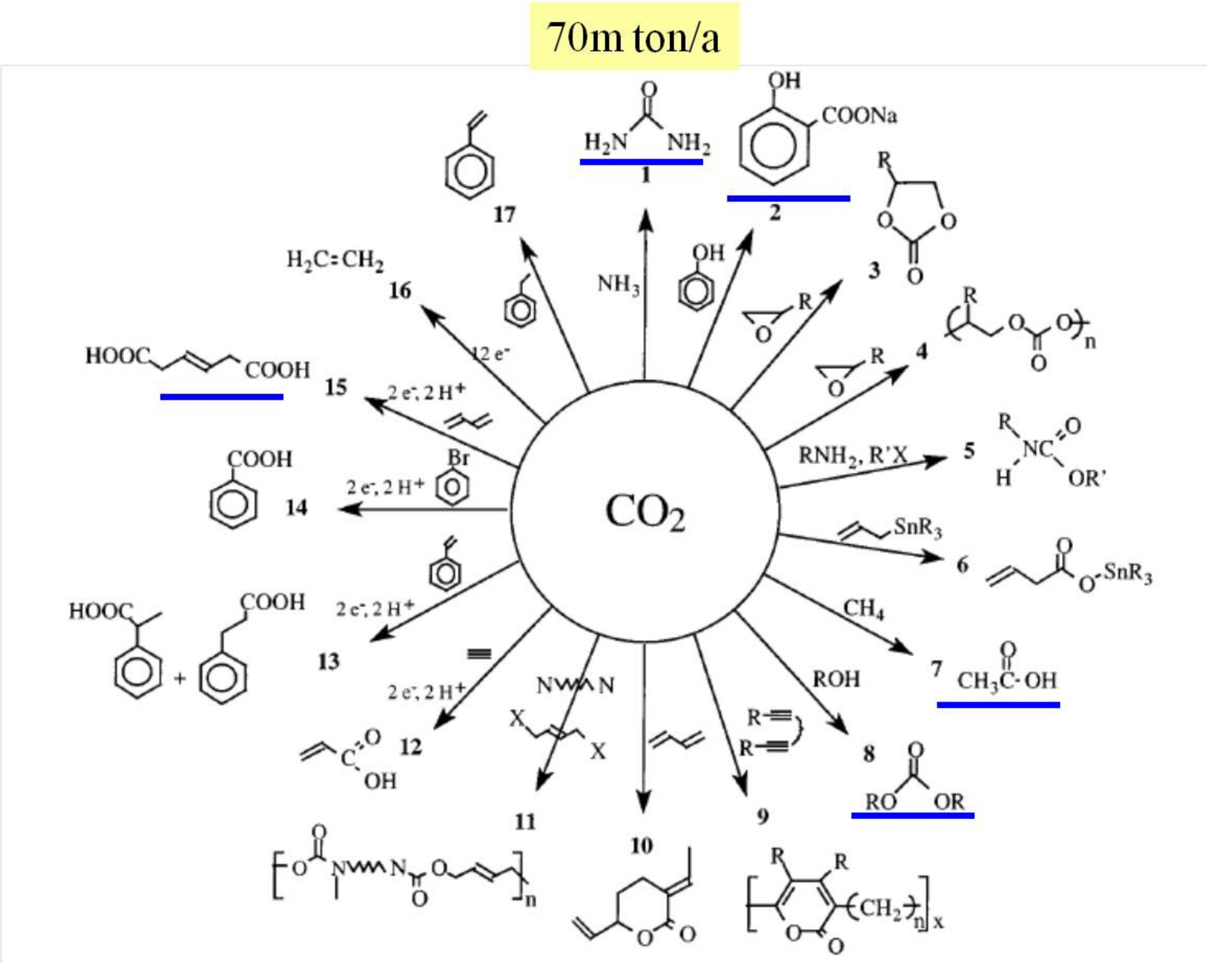

Fig 18 –some of the main ways for chemical reactions using CO2 as a raw material
Conference of Professor Xianhong Wang (EMRS/STOA 22 march 2011).

2.3.7. Transforming CO_2 into Polymer

CO_2 can also be the starting point in the synthesis of polymers such as PMMA, some polyether and polyethylene. Professor Xianhong Wang has developed such techniques and created several industrial plants in China. (Figure 20)

These techniques also have the edge of avoiding the manipulation of cyanhydric acid and sulfuric acid which represents considerable operational risks in traditional techniques we call that green chemistry (Figure 19)

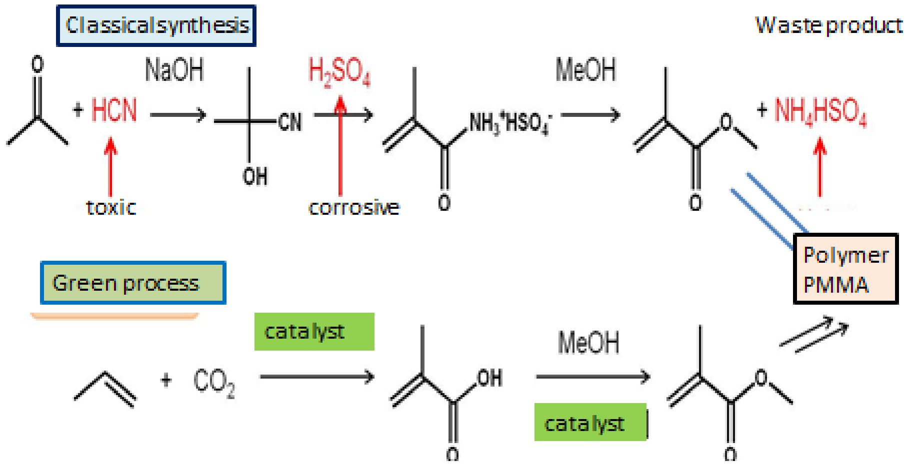

Figure 19 New route for polymer synthesis through green process

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Figure 20-Polymer product(polyester and polyether)from reactions of polyols with CO_2.
Process realized by Professor Xianhong Wang (CAS China).

(Laboratory of polymer ecomaterial, CAS /STOA 22/03/2011, Changchun Inst. Applied Chemistry, CAS)

The green chemistry is able to transform carbon dioxide as one of main resources for our future, many work from professor X.Wang are now starting in that field to open the way of a green chemistry.

Conclusion

We have to rethink CO_2 as key molecule.

The state of the art of science around carbon dioxide shows how deep is CO_2 involved in each life and energy cycle. Whether we look into energy production, energy storage, fuel synthesis, polymers creation or protein synthesis, Carbon and CO_2 have a critical role. The CO_2-H_2O pair is at the center of energy exchanges and present in all energy and life cycles.

CO_2-H_2O pair is to be thought as a critical pair that will be the center of energy storage and recycling processes as well as a key element to many chemical product synthesis which are at the core of our everyday life.

In the next fifty years, we expect an industrial transformation from fossil fuel use to carbon recovery compatible with our needs. Carbon dioxide is a key element of our civilization:It is key to life cycles and energy cycles and therefore critical to life and industry.

Bibliography

1. online .org CEN august 2010,2,p24
2. reducing carbon from coal: German projects C§EN 2010 sept 13 p 9
3. European Parliament STOA 22 march 2011
4. EMRS meetings: Paris Feb 2008;Strasbourg June 2009;Warsawsept 2011
5. Sciences 12 June 2009 vol 324 p 1389
6. Chem. Engineering Journal WWW .CHE.COM may 2008
7. Chemical Engineering Jan 2009 p 13)
8. Chemical Engineering, Dec. 2003, p. 7. Power span Conf. Portsmouth, NH, USA.
9. Book:Physics and Technology of High Current discharges in dense Gas Media and Flows Author:PhillipRutberg (Institute foe Electrophysics and electrical power (RAS)St Petersburg,Russia
10. CCS assessing economic Mac Kinsey 2009
11. Science 25 Sept 2009 Vol325 p 650...
12. Chemical Week May 3,2010,p25 Mitsui chemical
13. Science 18 April 2008 Vol 320
14. Science 323,1680 ,2009
15. Patent WO/2007/122498 D.Hildebrant,D.Glasser,B.Hansberger
16. Applied Catal.A, General, 172(1998)131-140 H.Habazaki, M.Yamasaki, B.- . P.Zhang;S.Kohno,T.Kakai,K.Hashimoto
17. C&EN Chemical & Engineering News.P. 34. July 26, 2010)
18. Source : ACS, 6 oct 2009)
19. Science, 23oct.2009, vol.326.
20. EnergyEnviron.Science, 2010, vol3, p.28
21. Professor Xianhong Wang Laboratory of polymer ecomaterial, CAS /STOA 22/03/2011, Changchun Inst. Applied Chemistry, CAS

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http://www.emrs-strasbourg.com/index.php?option=com_content&task=view&id=449&Itemid=1