CO_2 Capture for Chemical Use

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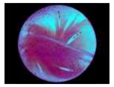
A bit about LGC

The LGC is a laboratory of **Chemical engineering**

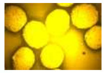


Electrochemical Processes

Process Systems Engineering

Research departments

Interface & Particle Interaction Engineering



bioprocesses and microbial systems

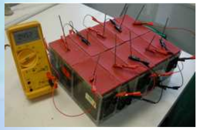
Reacting, Mixing & Separation

LGC and CO_2

Carbon Management is an inter-department research theme

Reduce Carbon intensity

- **Development of clean energy**


Microbial fuel cells

Biogas production of quality Natural Gas Vehicle

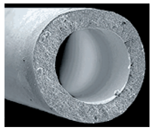

Production of syngas with biomass


Hydrogen production by electrolysis

- **Alternative process**

Carbon Capture and Storage

- **Development of new gas liquid contactor**


Hollow fiber membrane for pre and post combustion

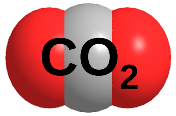

New packing in C/C for postcombustion capture


Packing optimization for O_2 production in oxycombsution

- **Modelisation and simulation of absorption CO_2 capture**

- **Development of new process for mineral carbonation**

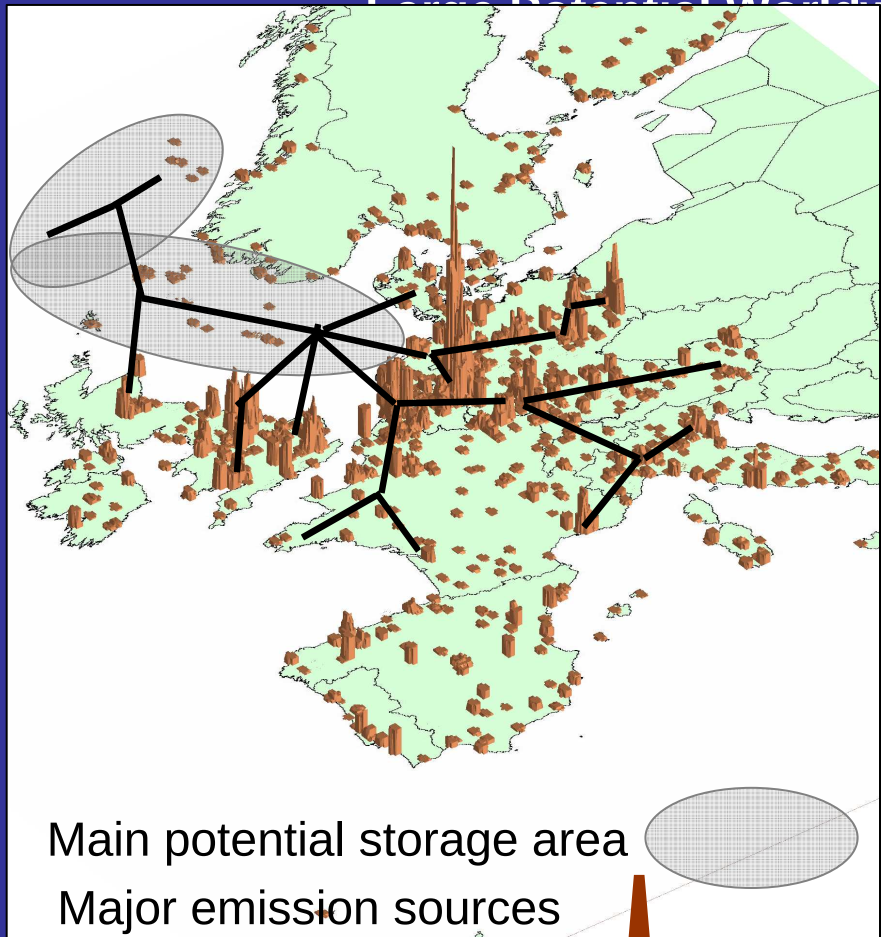
What happens after capture ?

?  ?

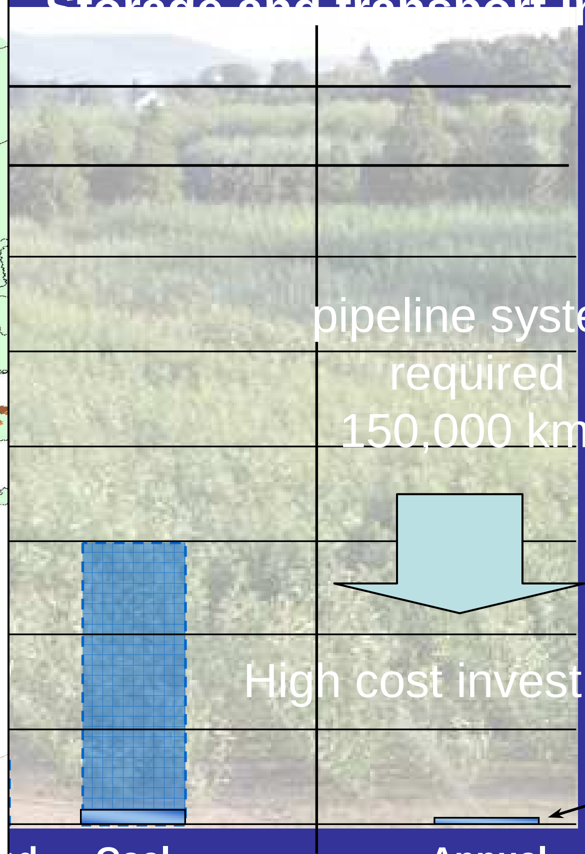
Storage

Large Potential Worldwide Storage Capacity

Storage and transport in Europe



K. Burnard, AEA Energy&Envr.



What happens after capture ?

? CO_2 ?

Storage

Large potential storage, problem of transport (decentralized option ?)

Valorization

Use
MT CO_2/Year

Direct use — ?

Chemical transformation

- Low-energy utilization — ?
  the entire CO_2 molecule is incorporated into the product
- High-energy utilization — ?
  Reduction of CO_2 via C-O bond cleavage — ?

Mineral Carbonation

Biological — ?

? = 30 GT CO_2/Year

Valorization

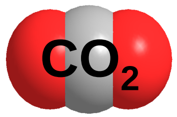
Direct use

Non toxic

Non-flammable

Renewable source

Thermodynamically and kinetics stable



Non-mutagenic

Non-carcinogenic

Easily handled

Not chemically inert but low reactivity

Direct used for numerous applications

- Fire extinguishers
- Mechanical industry (soldering, moulding)
- Waste-water treatment
- Food industry as an additive for beverages
- Food-packaging, …
- Supercritical solvent
- Enhanced oil recovery
- Spray gas
- Heat exchanger in nuclear plants
- Refrigerating agent (dry ice)

Valorization

Direct use

Estimated Use (*MT CO_2/Year*)

Enhanced oil recovery	40	*MT CO_2/Year*	*IPCC, **2005***
Other	13,5	*MT CO_2/Year*	*L. Dumergues **2008***
Total	**53,5**	***MT CO_2/Year***	

Advantages of direct use

+ Numerous applications
+ Safety and environmental benefits
+ General proximity of the producing and consumer sites of CO_2

Drawbacks of direct use

- Limited use compared to the overall CO_2 production (<0,02%)
- Need of high CO_2 purity

Industrial/research targets

- Increasing interest for CO_2 in refrigerating systems

  In France : 36 systems : supermarkets, freezing, cold store, ice cream, ice ring

  Research : Hydrates slurries good secondary refrigerant *L. Fournaison **2008***

- Developing EOR technologies

What happens after capture ?

? CO_2 ?

Storage

Large potential storage, problem of transport (decentralized option ?)

Valorization

		Use *MT CO_2/Year*
Direct use		55
Chemical transformation	Low-energy utilization: the entire CO_2 molecule is incorporated into the product	?
	High-energy utilization: Reduction of CO_2 via C-O bond cleavage	?
Mineral Carbonation		?
Biological		?

? = 30 GT CO2/Year

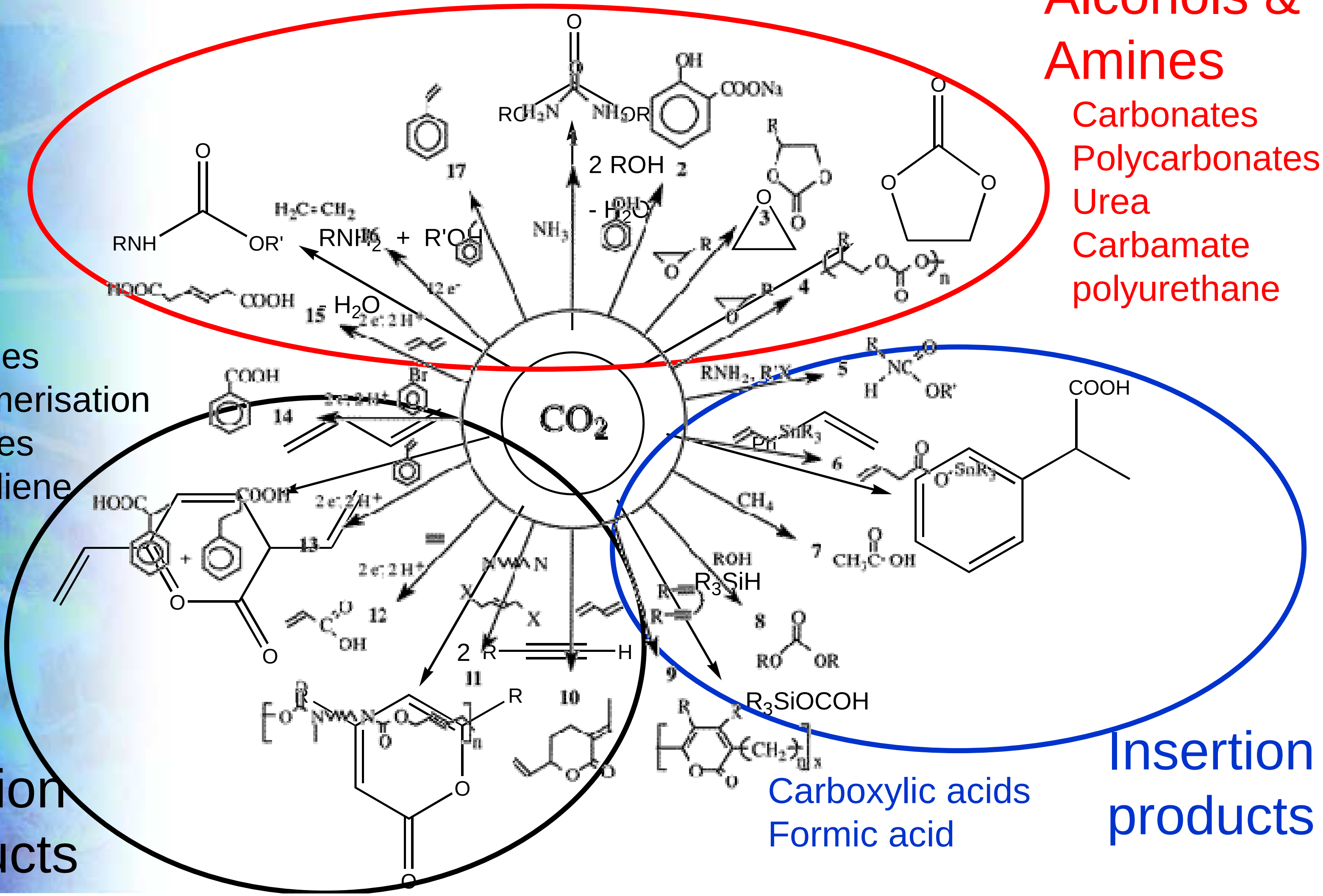
Valorization

Chemical transformation (Low-energy utilization)

CO_2 can react with a large number of substrates

Alcohols & Amines
- Carbonates
- Polycarbonates
- Urea
- Carbamate
- polyurethane

Alkynes
Polymerisation
Amines
butadiene



Addition products

Carboxylic acids
Formic acid

Insertion products

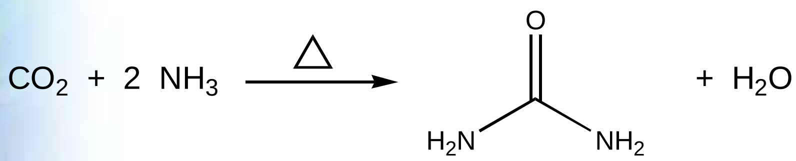
Valorization

Chemical transformation (Low-energy utilization)

Reactions manufactured : actually

use (CO_2)

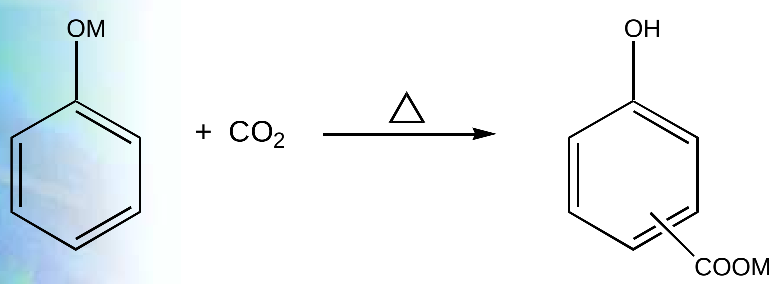
Urea (agricultural use)



70 MT/Year

*R.H. Heyn, SINTEF, **2008***

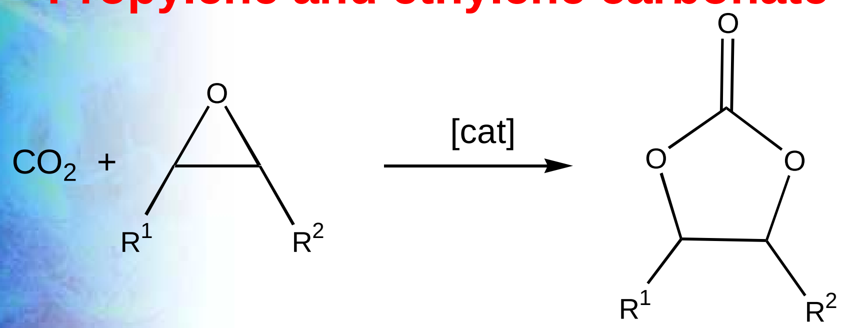
Hydroxybenzoic acids (Medicinal and cosmetic uses *-aspirine-*, food*)*



20 KT/Year

*R.H. Heyn, SINTEF **2008***

Propylene and ethylene carbonate (solvents, electrolytes)



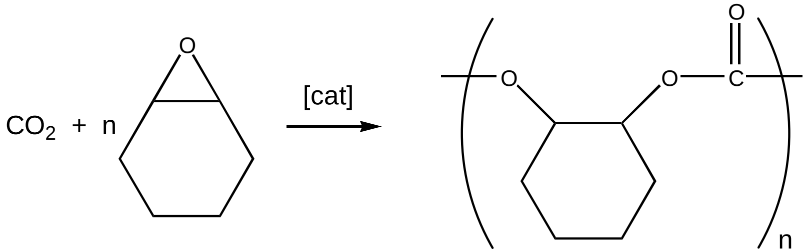
~ KT/Year

Valorization

Chemical transformation (Low-energy utilization)

Reactions developed : short term

Polycarbonates



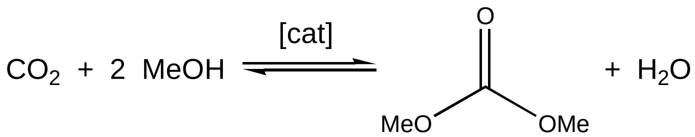
use (CO_2)

500 kT/Year

- toxic reactant avoided : phosgene
- Technology close to industrial implementation
- Process development under investigation

Darensbourg, D. J. Chem. Rev. ***2007***

Dimethylcarbonate (DMC)



50 kT/Year

M. Aresta, A. Dibenedetto, 2003

Reactions developed : medium and longer term

Carboxylic acids (pharmaceuticals, leather tanning, textile dyeing, plastics, lacquers, and solvents)

(alkyl)Carbamates (agrochemical, pharmaceutical)

Polyurethanes (foam)

Acrylic acids (reactant for polymer)

Valorization

Chemical transformation (Low-energy utilization)

Estimated Use (*MT CO_2/Year*)

Actually	100 *MT CO_2/Year*
Expected	<200 *MT CO_2/Year*
Total	**<300** ***MT CO_2/Year***

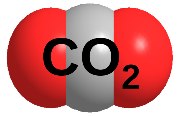
Advantages of Chemical transformation

- + Possibility to make valuable products (storage is a simple additional cost)
- + Several organic pathways for its activation and conversion
- + Use of more safe reactants, for ex. in substituting phosgene with DMC.
- + CO_2 adds value in developing sustainable (green) processes

Drawbacks of Chemical transformation

- – Limited use compared to the overall CO_2 production (<1%)
- – Need of high CO_2 purity
- – Catalyst development is necessary and essential

What happens after capture ?

?  ?

Storage

Large potential storage, problem of transport (decentralized option ?)

Valorization

Use
MT CO_2/Year

Direct use — 55

Chemical transformation
- Low-energy utilization — 300
  the entire CO_2 molecule is incorporated into the product
- High-energy utilization — ?
  Reduction of CO_2 via C-O bond cleavage

Mineral Carbonation — ?

Biological — ?

? = 30 GT CO2/Year

Valorization

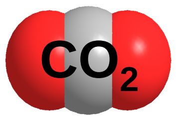
Chemical transformation (High-energy utilization)

Reduction of CO_2 via C-O bond cleavage

O = C = O

803 kJ/mol

Possible to synthetize a large variety of products
ranging from C1-type molecules to higher molecular weight



Fuels

CH_3OH, CH_4, CO

Catalytic hydrogenation

Electrochemical reduction

Valorization

Chemical transformation (High-energy utilization)

Catalytic hydrogenation

Methanol

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

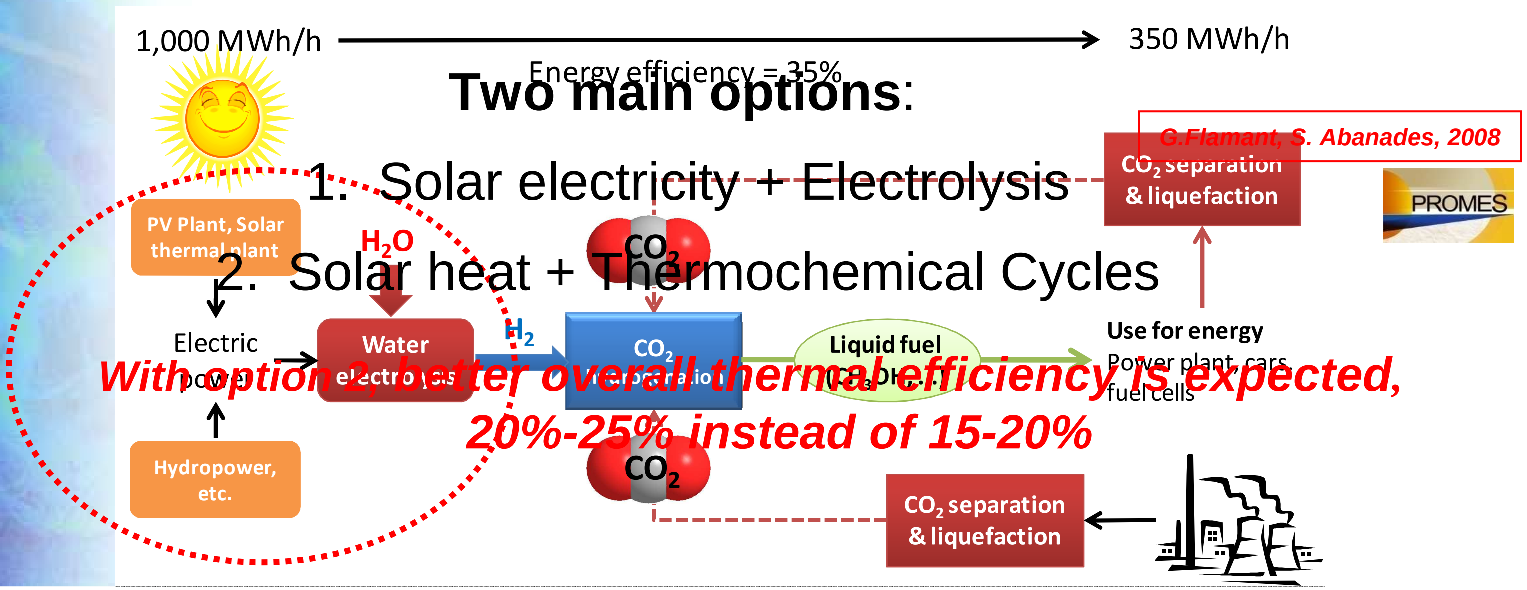
How much CO_2 produced per H_2?

- Mitsui Chemicals (Japan) will build a demonstration plant (100 T/yr Methanol)

  -better catalysts has to be developed
  -Expects to emit half as much CO_2 as consumed

- The problem is the availability of hydrogen or of hydrogen sources

- Technology proposed development by NITE/RITE (Japan) using renewable energy sources



G.Flamant, S. Abanades, 2008

Two main options:

1. Solar electricity + Electrolysis
2. Solar heat + Thermochemical Cycles

With option 2, better overall thermal efficiency is expected, 20%-25% instead of 15-20%

Valorization

Chemical transformation (High-energy utilization)

Electrochemical reduction

Water Reduction

$$2H_2O \longrightarrow 4H^+ + 4e^- + O_2$$

CO_2 Reduction

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad -0.53\ V$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad -0.48\ V$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad -0.38\ V$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad -0.24\ V$$

Energy ?

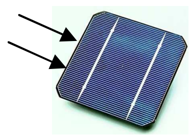
Valorization

Chemical transformation (High-energy utilization)

Photo- and electro- chemical/catal. conv. CO_2

Indirect use of solar energy : PhotoElectroChemical reduction

Two steps



photovoltaic cell

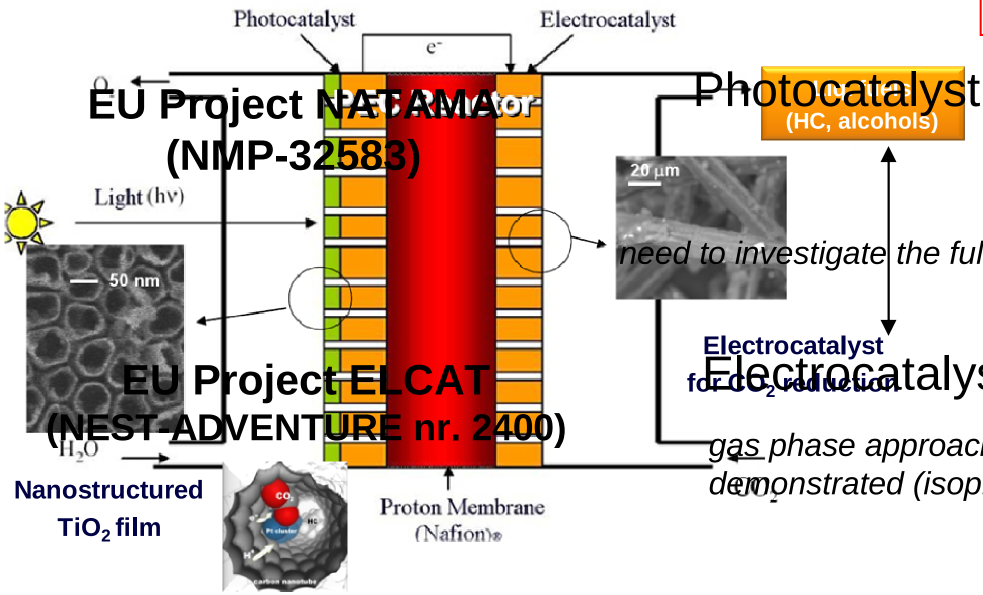
→ electricity → e^- ⇨ reduce electro-chemically/catalytically CO_2 in a physically separate cell

One step

coupling the two processes in a single unit PhotoElectroChemical (PEC) Reactor

G.Centi, 2008

Recent research



EU Project NATAMA (NMP-32583)

EU Project ELCAT (NEST-ADVENTURE nr. 2400)

Photocatalyst part

need to investigate the full PEC system

Electrocatalyst part

gas phase approach has been demonstrated (isopropanol)

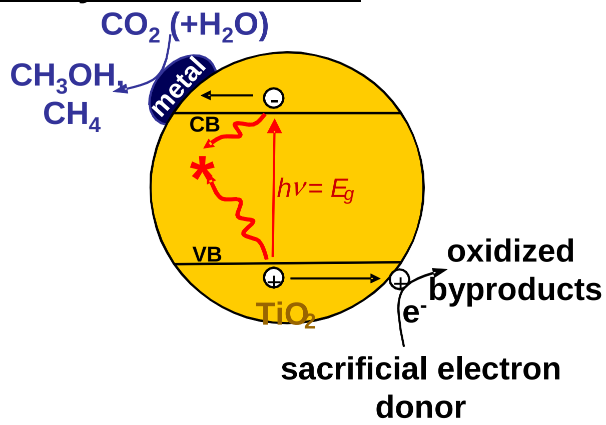
Valorization

Chemical transformation (High-energy utilization)

Photo- and electro- chemical/catal. conv. CO_2

Direct use of solar energy : Photocatalytic reduction

Natural photosynthesis



Artificial photosynthesis

Linsebigler et al., Chem. Reviews, 1995

But still a challenge :

- Limited productivities in the absence of sacrificial agents
- Low solubility of CO_2 in water
- CO_2 photoreduction process is competing with H_2 and H_2O_2 formation
- Need of UV lamps (low activity in visible region)

G.Centi, 2008

Valorization

Chemical transformation (High-energy utilization)

Estimated Use (*MT CO_2/Year*)

Actually	0	*MT CO_2/Year*
Expected	*limitless*	*MT CO_2/Year*

Advantage of CO_2 conversion into fuel

+ Large potential to reduce greenhouse gas emissions
+ Recycled CO_2 using renewable resources contributing to close the carbon-cycle on actual infrastructure .
+ Use the solar energy (and water) to convert CO_2 into fuels which may be easy stored and transported

Drawback of CO_2 conversion into fuel

- Need long term developments (process improvement needed, not experimental units)
- Not solve the problem of greenhouse gas in the next future

What happens after capture ?

? CO_2 ?

Storage

Large potential storage, problem of transport (decentralized option ?)

Valorization

		Use *MT CO_2/Year*
Direct use		55
Chemical transformation	Low-energy utilization the entire CO_2 molecule is incorporated into the product	300
	High-energy utilization Reduction of CO_2 via C-O bond cleavage	*Large potential (in futur)* ?
Mineral Carbonation		
Biological		?

? = 30 GT CO2/Year

Valorization

Mineral Carbonation

The chemical fixation of CO_2 in minerals to form geologically stable mineral carbonates

$$(Mg, Ca)_x Si_y O_{x+2y} + x\,CO_2 \rightarrow x\,(Mg, Ca)CO_3 + y SiO_2$$

(X, Y depends of minerals : Calcium , Magnesium , Wollastonite, Olivine, Serpentine)

Different ways

Solid-Gas Reaction
~1% conversion efficiency

Aqueous Mineral Carbonation
costly reaction conditions (185 ℃ and 115 atm)

Multi-stage Aqueous Mineral Carbonation
reduced conditions, but acidic medium incurs cost

Single-Stage Aqueous Mineral Carbonation

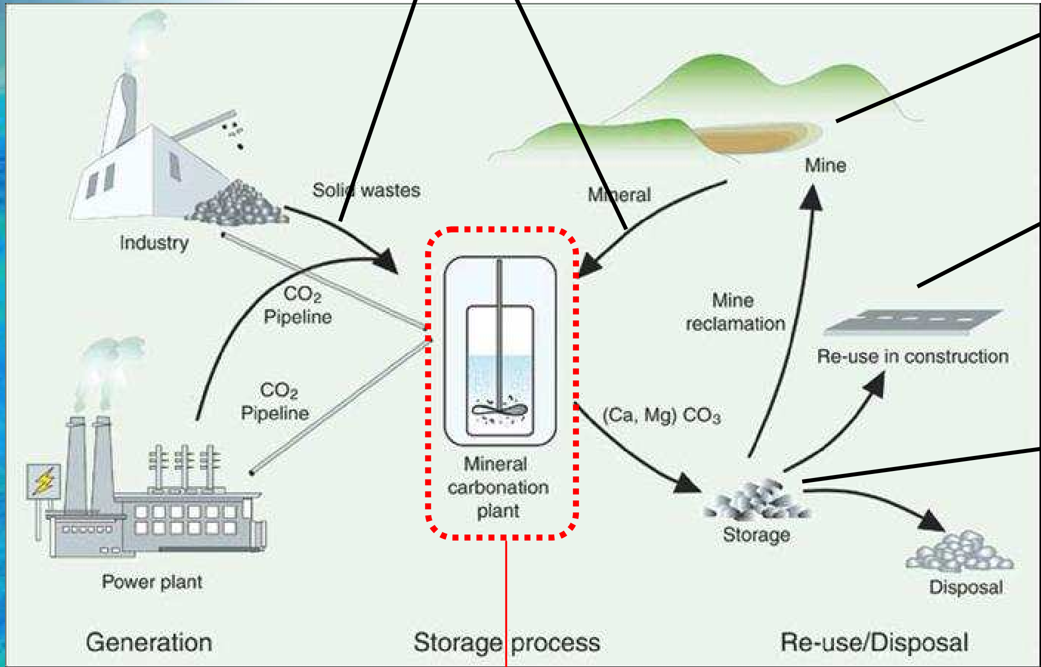
Valorization

Mineral Carbonation

Different mining residues/byproducts can be used to sequester CO_2.

There are enough minerals to potentially capture all the emitted CO_2 (> 1 000 000 Gt CO_2).

Lackner et. al, 1998



Energy Research Centre of the Netherlands (ECN)

Carbonates are potentially usable as construction materials.

Carbonates are the most stable form of carbon dioxide storage

Recent research : Single or Multi-Stage Aqueous Mineral Carbonation

Problem of dissolution and precipitation in the reactor
Mineral characterization
Bio mineral carbonation
Implementation of industrial pilots

Carmex

Valorization

Mineral Carbonation

Estimated Use (*MT CO_2/Year*)

Actually	0	*MT CO_2/Year*
Expected	*limitless*	*MT CO_2/Year*

Advantage of CO_2 mineral carbonation

+ Large potential storage
+ Permanent and inherently safe sequestration of CO_2 by mineral carbonation
+ Valorization of the final products
+ Existing technologies (more maturity of mineral carbonation than CO_2 into fuel)

Drawback of CO_2 mineral carbonation

- Sequestration costs of current mineral carbonation technologies (> 100€/ton CO_2)
- Not enough experimental units and process improvement needed

What happens after capture ?

? CO_2 ?

Storage

Large potential storage, problem of transport (decentralized option ?)

Valorization

Use
MT CO_2/Year

→ Direct use — 55

→ Chemical transformation

- Low-energy utilization — 300
  the entire CO_2 molecule is incorporated into the product
- High-energy utilization — ***Large potential (in futur)***
  Reduction of CO_2 via C-O bond cleavage

→ Mineral Carbonation — ***Large potential (cost)***

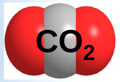
→ Biological — ?

? = 30 GT CO2/Year

Valorization

Biological

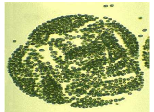
CO_2 conversion into mirco-algae by photosynthetic microorganisms



Closed photobioreactor

Open photobioreactor

Valorization of microalgae



Microalgae

Efficient photosynthesis
Potential for intensive cultures
High growth rate

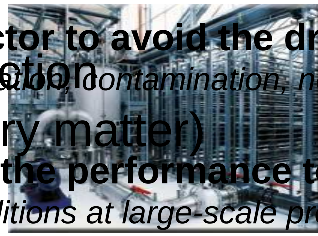
biofuel
biogaz
food for livestock,
chemicals,
colorants,
perfumes,
vitamins,
Etc.

Major part of actual production
(No temperature control, evaporation, contamination, no intensification)
(10 000 tons per year of dry matter)

Culture of *Haematococcus pluvialis* for the production of astaxanthine (20000 l on a 100 m² area**) - Mera Pharmaceuticals - Hawaii).**

Actual research

Develop closed photoreactor to avoid the drawback of open photoreactor



Culture of *Chlorella vulgaris* in greenhouse of 2000 m² (500 kms of glass tube, volume of 700 m3).
System commercialised by B. Braun Biote International GmbH (BBI).

Needs to improve the performance to be cost-effective:
(control of culture conditions at large-scale production, use of solar flux, energetic consumption, management of the inputoutput)

Global CO_2 consumption → 10 Mt/year

J. Legrand, J. Pruvost ***2008***

JP Cadoret ,O.Bernard ***2008***

b-*carotène - **Australia***

Valorization

Biological

Estimated Use (*MT CO_2/Year*)

Actually	10	*MT CO_2/Year*
Expected	✗ *2 every 5 years*	*MT CO_2/Year*

van Harmelen & Oonk, **2006**

Advantage of biological conversion

+ The production of microalgae increase around the world
+ Simple conception and low investment cost for open photoreactor
+ Large valorization of microalgae
+ Great diversity (>30,000 species) of microalgae able to metabolize other gas : NO_X, SO_X

Drawback of biological conversion

- Limit production exist : theory limit 400 T/ha/year and current productivity 30 T/ha/year
- There will never be enough surface for a significant consumption of CO_2
- Microalgae are sensitive : cold, strong illumination
- No knowledge of the economic aspects

Conclusion

Direct used and chemicals conversion (low energy) is NOT a solution to the Greenhouse Effect

The volume of CO_2 used cannot increase from the actual about 0.5% to over 1-2%.

Safety and environmental benefits related to the use of more safe reactant

Fundamental catalysis research is required

A larger contribution to the reduction of CO_2 emissions could derive by converting CO_2 back to fuels.

Need long term development

Large potential of CO_2 conversion by mineral carbonation

Need experimental units and process improvement