
UNIVERSITY OF
BATH
Michele Aresta
Dreams
A Vision
Facts
Lectio Magistralis delivered at
The Bath University on the day
October 5th, 2016

The University of Bath commemorates 50 y since its foundation.

Even if quite young it has reached a prestigious position in UK and the world.

Ad majora!

Dedicated to….

- My Family: Raffaella
  Gianluca, Brunella, Manuela
- My undergraduate and graduate Students
- My Post-Docs
- All Co-authors
- My former students and now Colleagues:
  Eugenio Quaranta, Immacolata Tommasi,
  Angela Dibenedetto
- The University of Bath and You

Thanks

To all funding agencies: MIUR, UNIBA, EU (FP4,6,7), ENIChem, ENI, TOTAL, ARKEMA


BARI
North Atlantic Ocean
North Sea
Baltic Sea
Mediterranean Sea
Bay of Biscay
English Channel
Irish Sea
Tyrrhenian Sea
Adriatic Sea
Ionian Sea
Aegean Sea
Black Sea
Gulf of Finland
Skagerrak
Strait of Gibraltar
Sardinia
Corsica
Sicily
Balearic Islands
Rockall (U.K.)
Shetland Islands
Orkney Islands
Hebrides
Aland Islands
Gotland
Oland
Bornholm
Isle of Man (U.K.)
Guernsey (U.K.)
Jersey (U.K.)
Tagus
Loire
Elbe
Vistula
Danube
Dniepr
Dniester
Volga
Oslo
Bergen
Gävle
Stockholm
Helsinki
St. Petersburg
Tallinn
ESTONIA
RUSSIA
LATVIA
Riga
LITHUANIA
Vilnius
Kaliningrad
RUSSIA
Smolensk
Minsk
BELARUS
Gdańsk
Warsaw
Brest
Kiev
Poznań
POLAND
Wrocław
Kraków
L'viv
UKRAINE
Rostock
Hamburg
Berlin
Amsterdam
NETHERLANDS
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GERMANY
Leipzig
Bonn
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Brussels
BELGIUM
Luxembourg
LUX.
Stuttgart
Munich
Prague
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SLOVAKIA
BRATISLAVA
MOLDOVA
Chişinău
Odesa
Vienna
AUSTRIA
Graz
Budapest
HUNGARY
Cluj-Napoca
ROMANIA
Bucharest
Constanta
Pécs
Ljubljana
SLOVENIA
Zagreb
Belgrade
Serbia
BOSNIA AND HERZEGOVINA
Sarajevo
CROATIA
Varna
BULGARIA
Sofia
Podgorica
Montenegro
Skopje F.Y.R.O.M.*
Tirane
ALB.
Istanbul
Thessaloniki
TURKEY
Ioánnina
Corfu
GREECE
Athens
Peloponnisos
Rhodes
Crete
Le Havre
Paris
Nantes
Strasbourg
FRANCE
SWITZ.
Bern
LIECH.
Geneva
Lyon
Bordeaux
Bilbao
Porto
PORTUGAL
SPAIN
Madrid
Barcelona
ANDORRA
Lisbon
Valencia
Sevilla
Málaga
Gibraltar (U.K.)
Ceuta (SPAIN)
Melilla (SPAIN)
Algiers
Tunis
Valletta
Palermo
Milan
Venice
Turin
Genoa
Florence
SAN MARINO
MONACO
Marseille
ITALY
Rome
VATICAN CITY
Napies
Scale 1:19,500,000
Lambert Conformal Conic Projection,

Pills of History

Remains of a human settlement dated at 3500 bC in Bari area

Most large cities were founded btw 800 and 650 bC

Apuli

Dauni

FOGGIA

BARI

Peuceti

Calabri

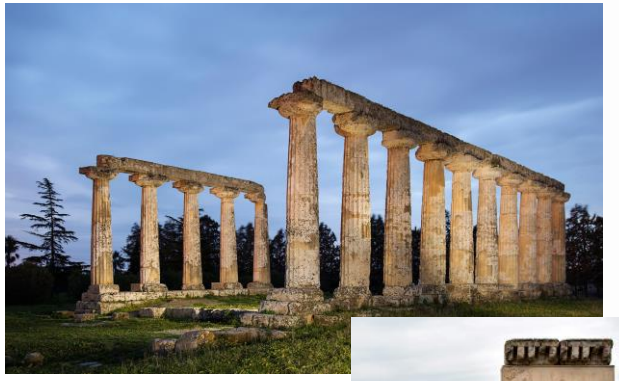
TARANTO

BRINDISI

LECCE

Messapi

The Altamura Man
125 000 years old



Magna Grecia
650-207 bC


www.copugliq.it

Some more history notes

Roman Province
207 bC-500 aC

Bizanthine since
507
Arab Emirate
841-871 aC

Norman Swabian
Domination
from ca 950 until 1260

Castel del Monte

Hunting Castle?
Astronomical studies?

Built in 1230
by Frederick II
Swabian
(1194-1250)
King of Italy

Saint Nicholas Basilica 1087-1100

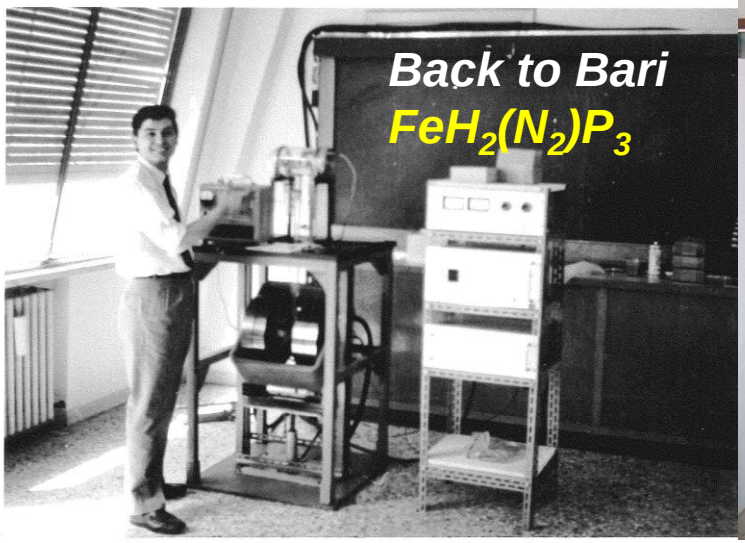
- **The Spanish domination in XIII-XVI centuries and afterwards until of the end XVIII century linked Bari to Naples and Palermo**

- **After Italy unification 1860 and until 1950 the economy was based on agriculture, food industry (first for the production of hard wheat), fishing, briding. Industrialization (steel, cement, refineries, agro-food) was started after 1950!**
- **Now, the tertiary is the main activity, followed by agriculture (1° for oil, 2° for wine production) and industry (large industries are being replaced by SMEs in the HiTech, Avio and Biotech areas).**
- **Tourism is gaining positions: in 2015 over 3 Mpersons toured in Apulia, with a share of >25% foreign people.**


www.copuglia.it


PRIMITIVO
CARVINEA
NEGROAMARO
CARVINEA
NERO DI TROIA
GRIFO

University of Milan



To Bari again

From Dinitrogen Fixation

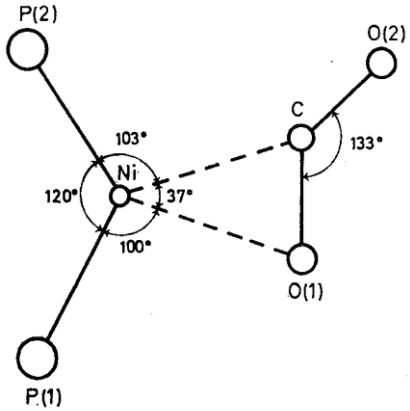
to

Carbon Dioxide Utilization

CO_2 is a resource, it is not a waste…

New Nickel–Carbon Dioxide Complex: Synthesis, Properties, and Crystallographic Characterization of (Carbon dioxide)-bis(tricyclohexylphosphine)nickel

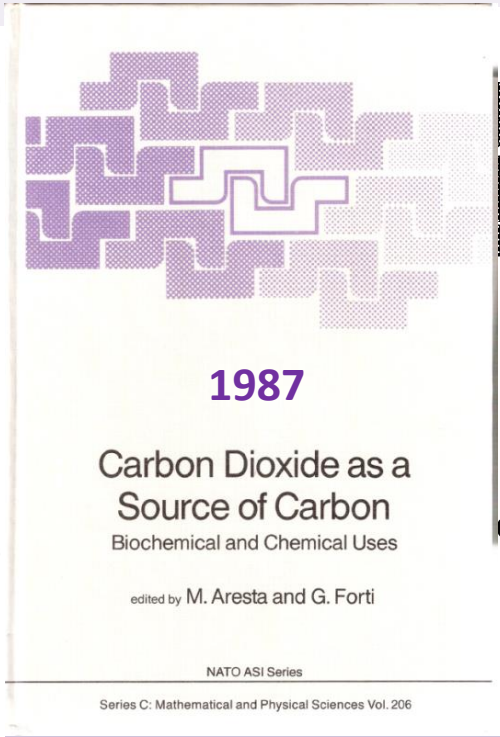
By Michele Aresta and C. Francesco Nobile
(*Istituto di Chimica Generale ed Inorganica, Università, Via Amendola* 173, 70126 *Bari, Italy*)
and Vincenzo G. Albano, Elisabetta Forni, and Mario Manassero
(*Istituto di Chimic* 20133 *Milano Italy*)

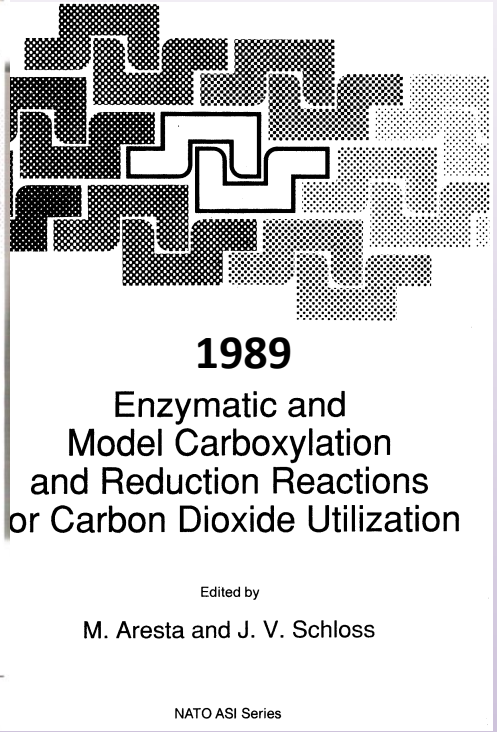


Reprinted from

Journal of The Chemical Society
Chemical Communications
1975

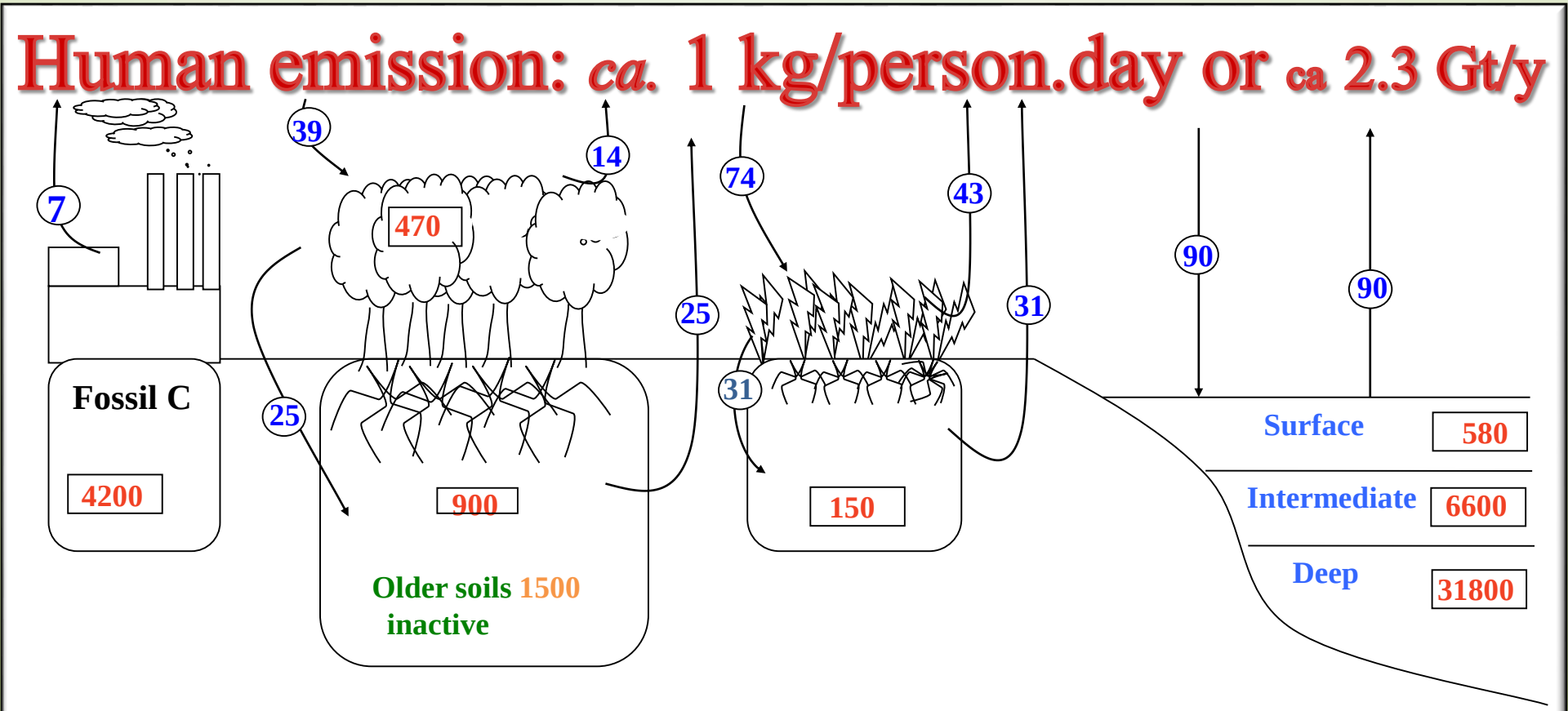
The Chemical Society, Burlington House, London W1V 0BN





ICCDU running since 1991

The natural C-Cycle

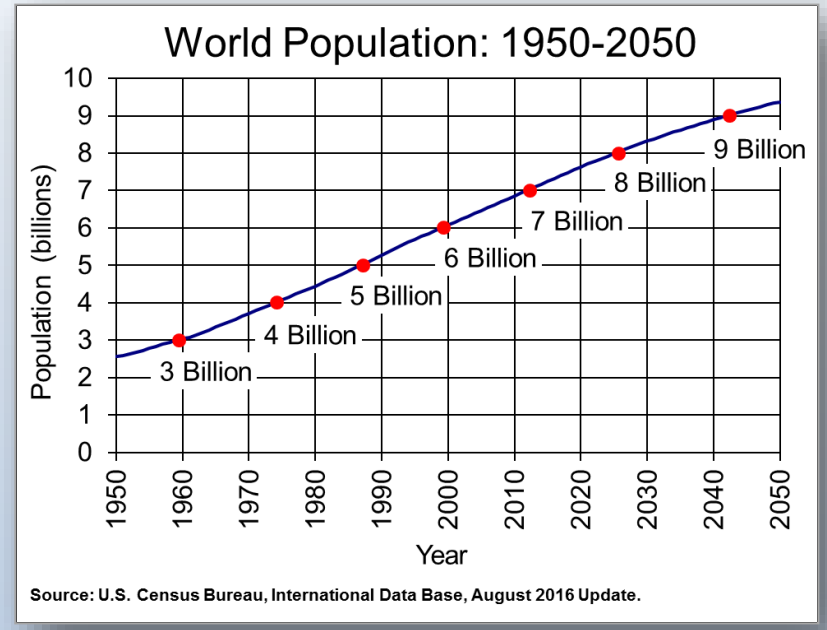


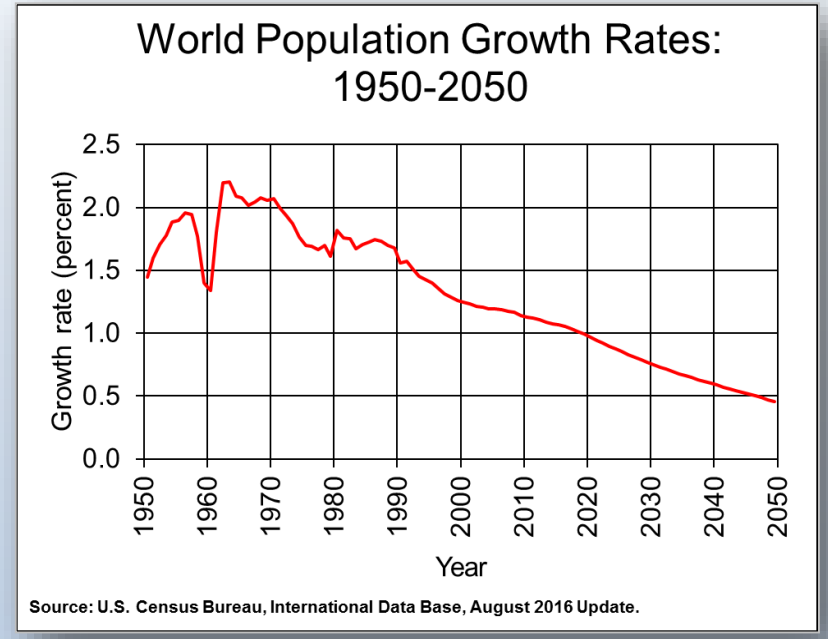
A recent estimate has set at 1 020 Gt/y the amount of converted CO_2

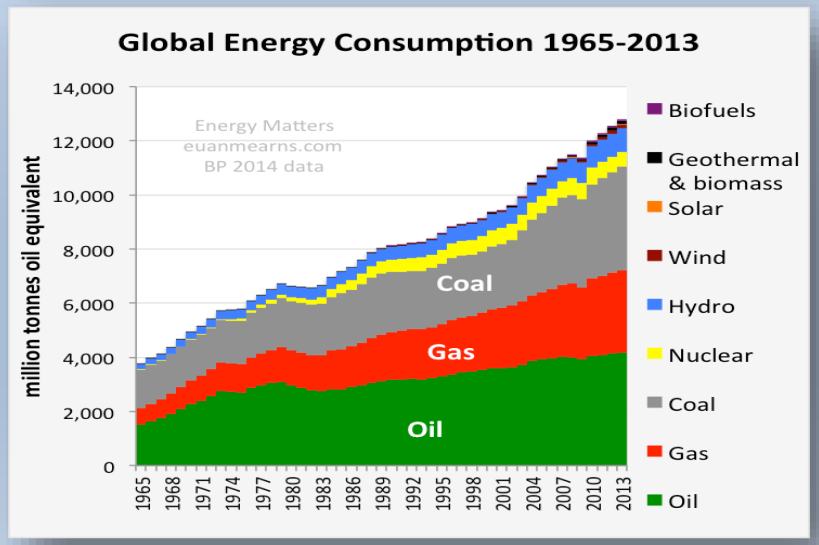
FOSSIL FUEL | **TERRESTRIAL BIOSPHERE** | **OCEAN**

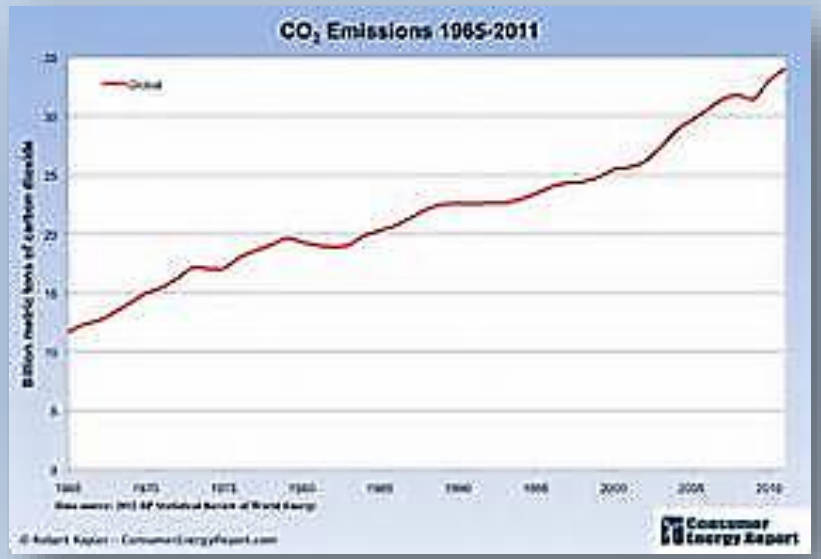
residential in **GtC**; fluxes in **GtC per year**

Society, Energy, and CO_2



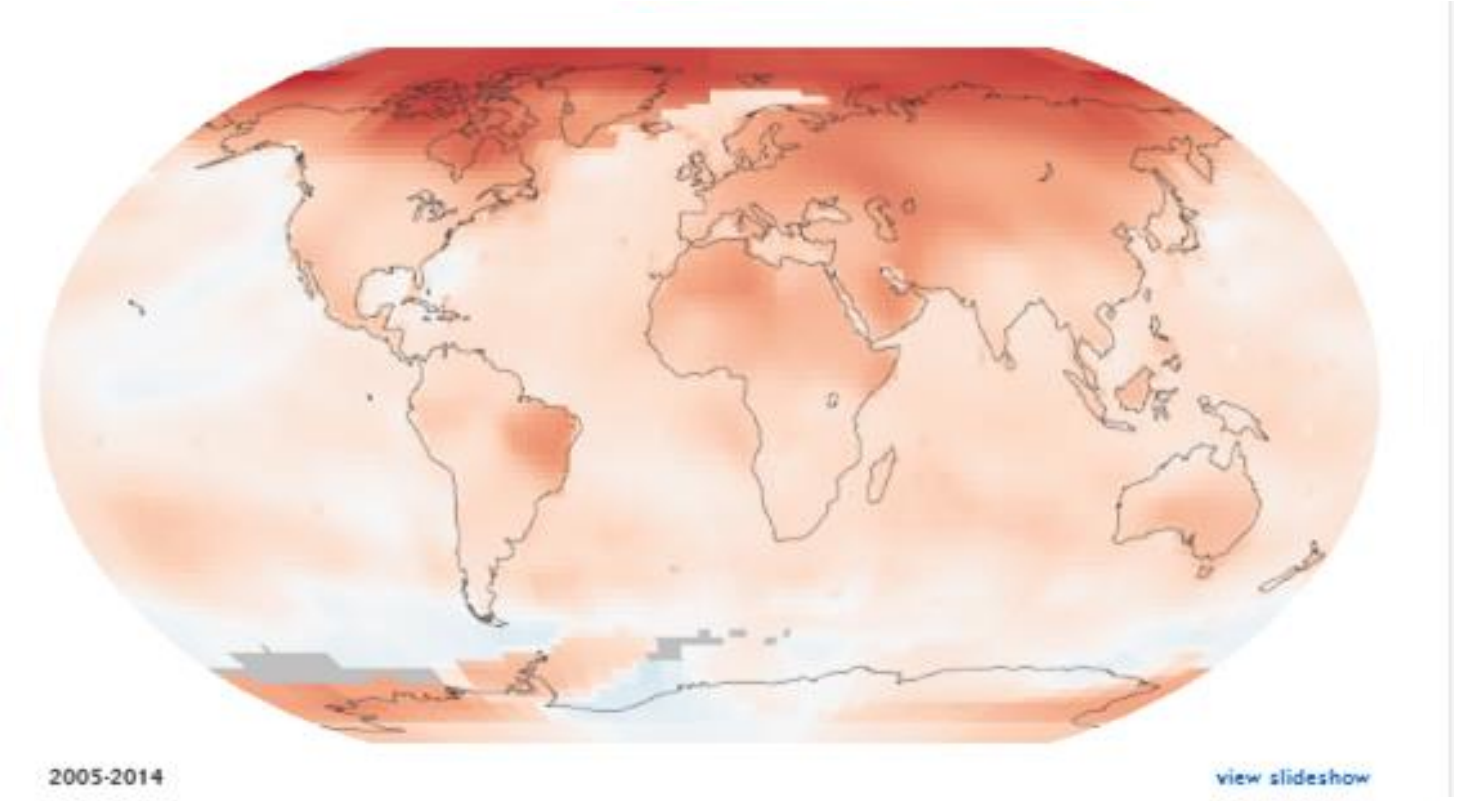






Global warming from 1880 to 2013

As of 2014, 2013 tied with 2009 and 2006 for the seventh warmest year since 1880 according to NASA scientists. With the exception of 1998, the 10 warmest years in the 134-year record have all occurred since 2000, with **2010** and **2005** ranking as **the warmest years on record**.



COP21, Paris 2015

- Article 7 of the Draft clearly states the role of:
  - *Technology deployment and dissemination for implementation of mitigation and adaptation*
  - *Strengthening cooperative actions on technology development and transfer for improving resilience to CC and reducing greenhouse gas emissions.*
- The Draft Proposal recognizes the key role of a "*vision for innovation*" and states that accelerating, encouraging, and enabling innovation is critical for an *effective long-term global response to climate change and promoting economic growth and sustainable development.*

Need of stepping from the linear...

Take…Use…Dispose

RESOURCE EXTRACTION → PRODUCTION → DISTRIBUTION → CONSUMPTION → WASTE

...to the circular-C economy

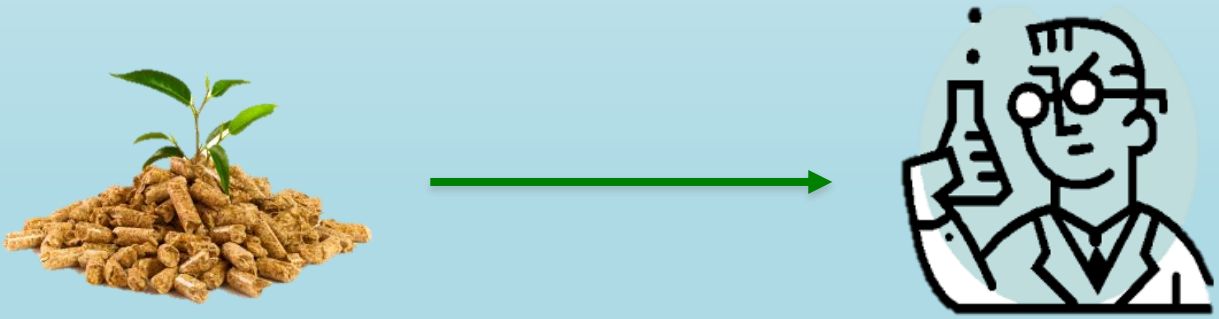
Alternative to fossil-C: Carbon-recycling, a must for the future

Strategies:

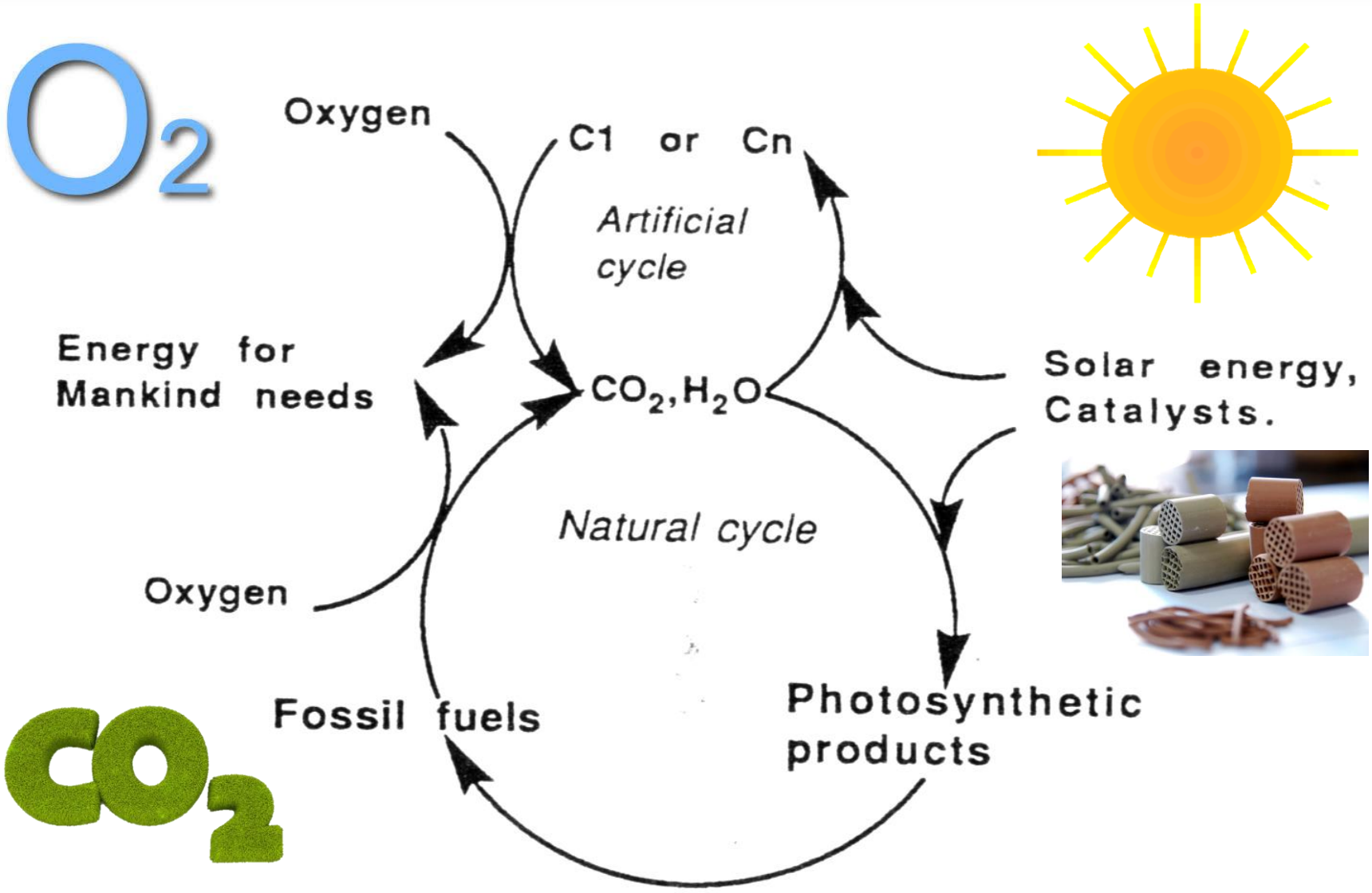
- **Direct conversion of Carbon Dioxide:**

  Carbon Dioxide Capture and Utilization-CCU

- **Let Nature fix CO_2 and Chemistry convert biomass (terrestrial and aquatic) into chemicals, materials and fuels**



- **Integration of Chemistry and Biotechnology**

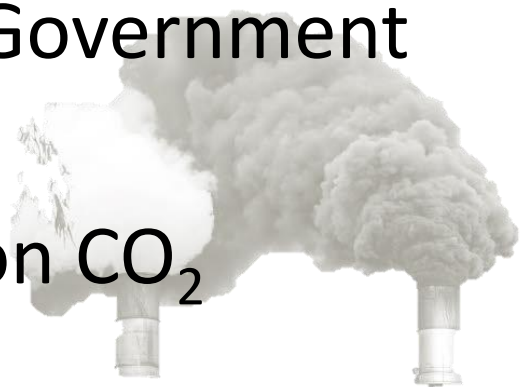


M. Aresta in "Enzymatic and Model carboxylation and reduction reactions for carbon dioxide utilization", M. Aresta and J.V. Schloss Eds, Kluwer Acad Publ, NATO ASI Series C 314 (1990) 1-42

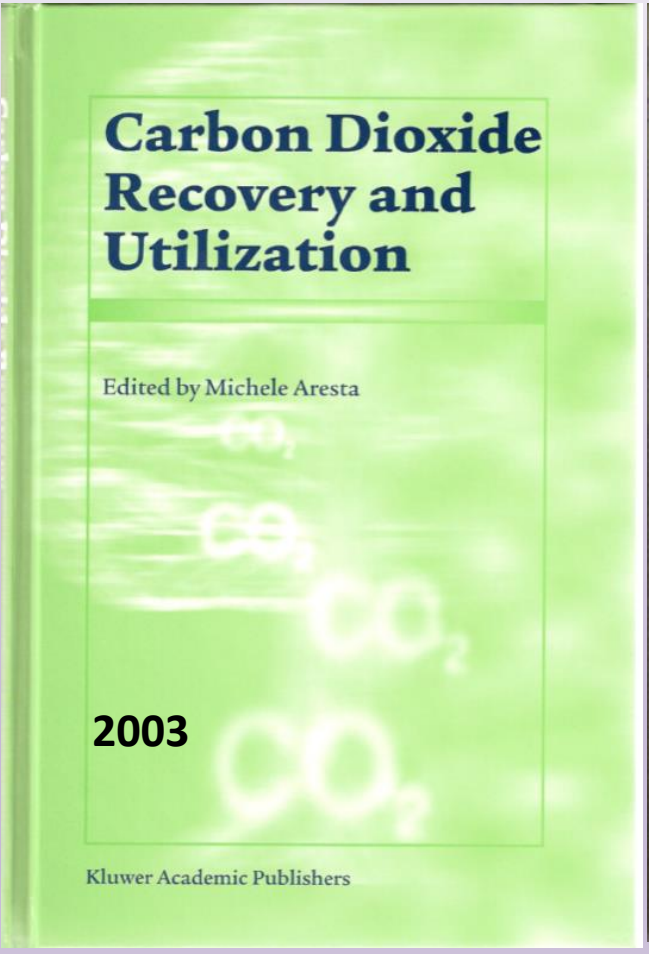
CO_2 and the italian government

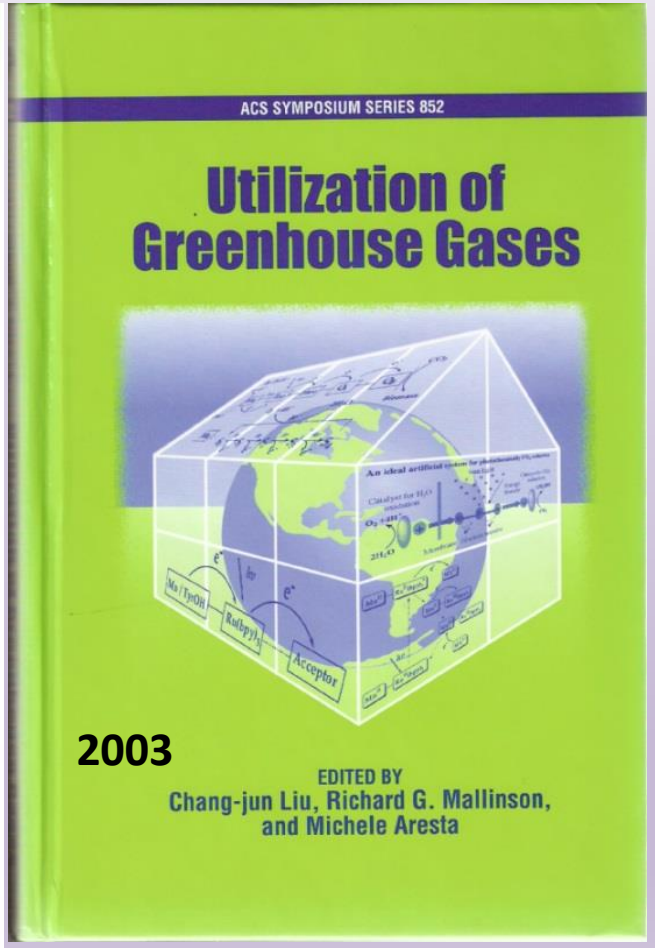
- 1985 Letter to the Ministry of University proposing the Italian Research Center for Carbon Management
- 1989 Proposal to CNR of a Center on CM
- 1990 Organization of the Italian Group for CM

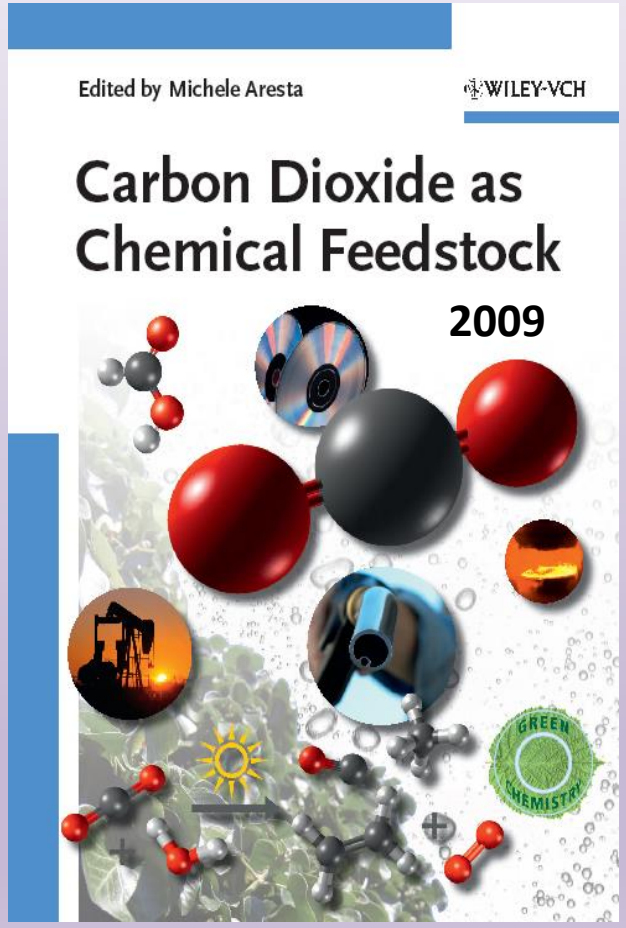
  Participation in the IEA GHG Programme
- 1991 The Italian Institute for CM was agreed
- 1992 The fall of the Government cancelled all achievements: "CM is not a Government issue, but of those who emit CO_2"
- 1998 RUCADI, the first EU Project on CO_2



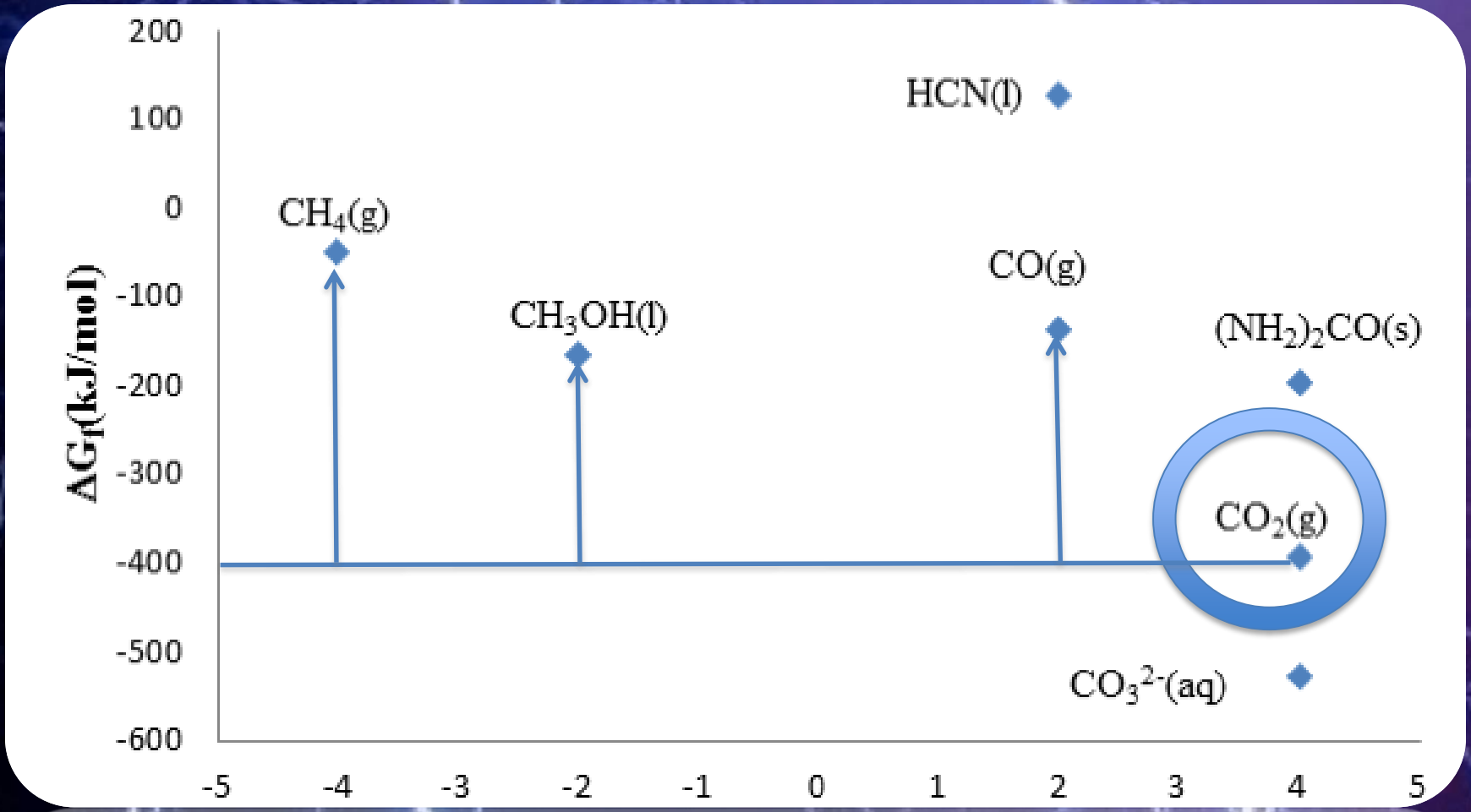
Carbon Dioxide Recovery and Utilization RUCADI FP4 1998-2002



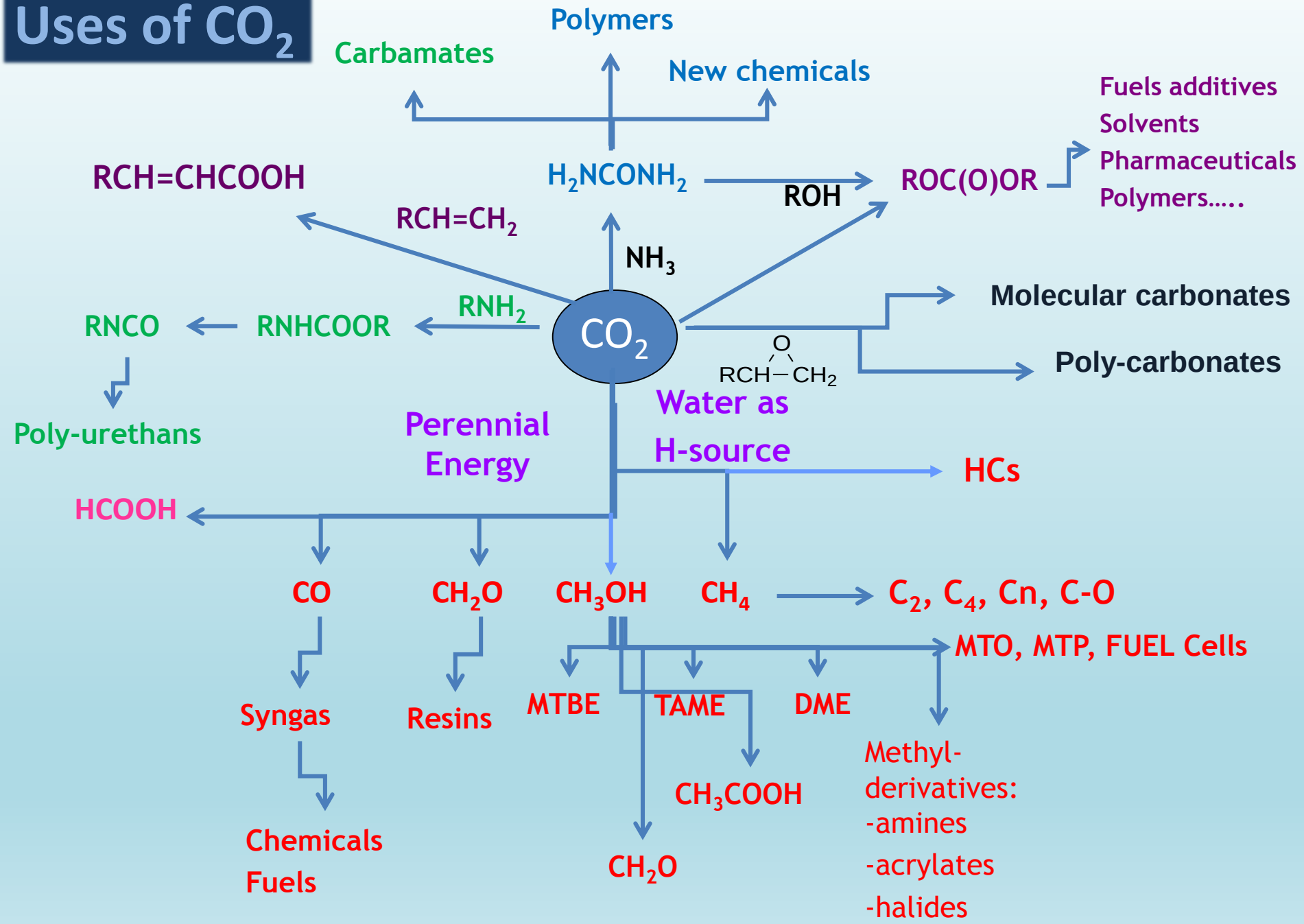




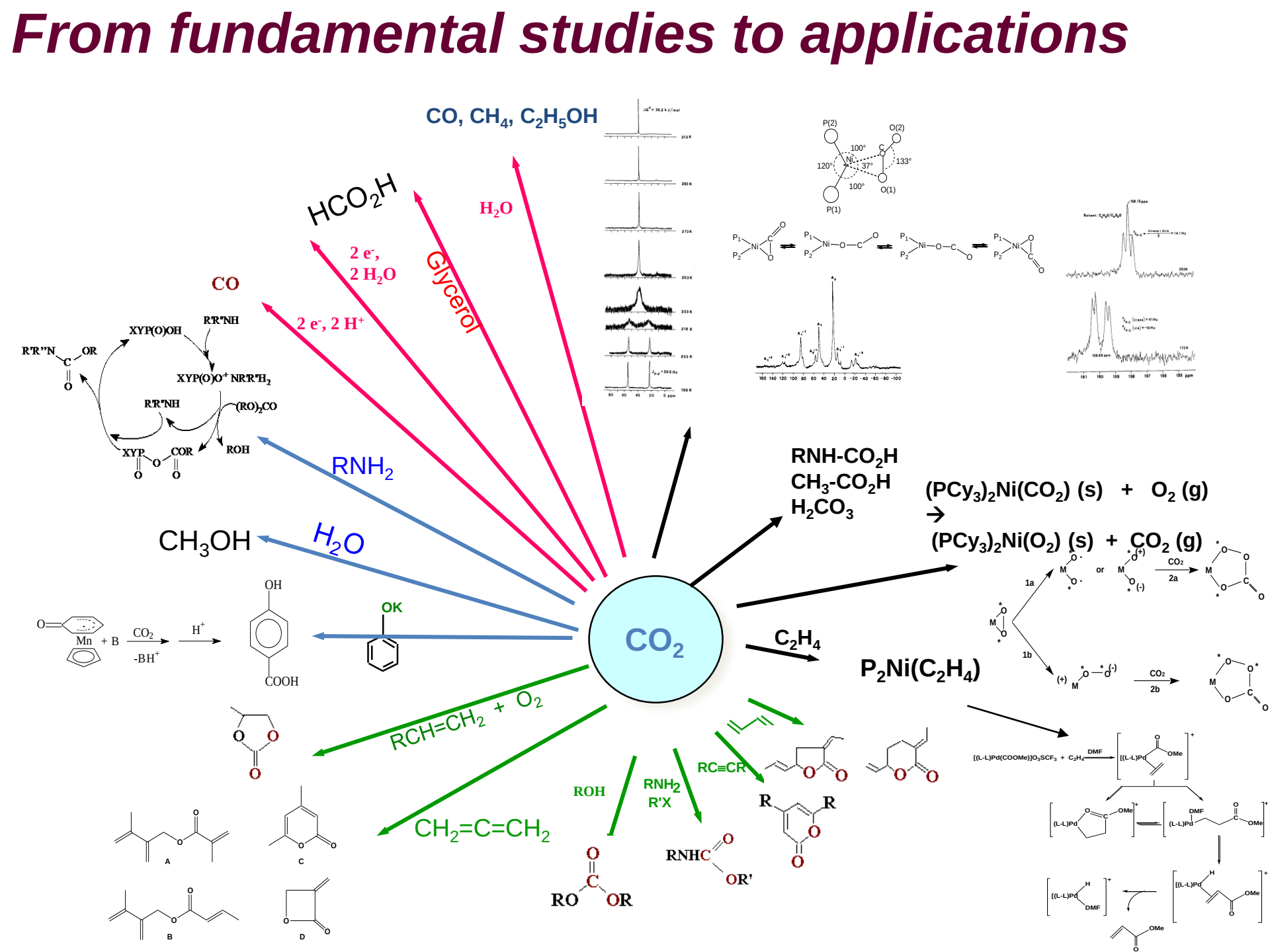
Energy issues



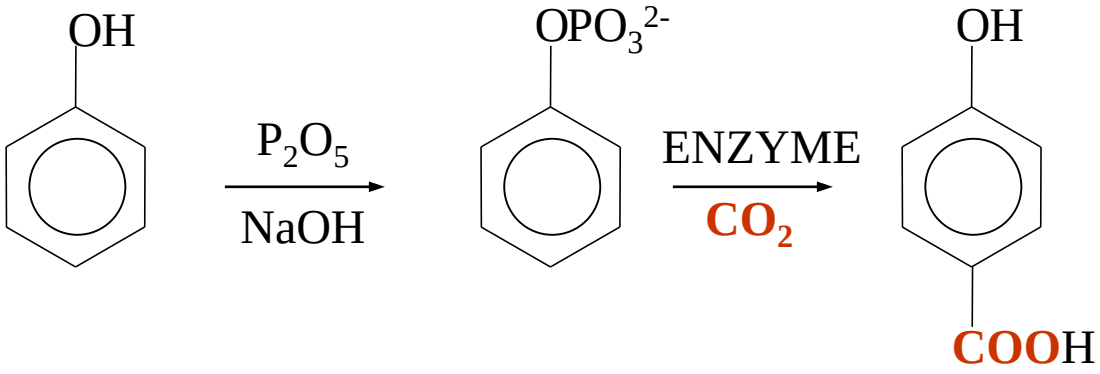
Uses of CO_2


Polymers
Carbamates
New chemicals
Fuels additives
Solvents
Pharmaceuticals
Polymers…..
RCH=CHCOOH
H_2NCONH_2
ROC(O)OR
ROH
$RCH=CH_2$
NH_3
Molecular carbonates
RNCO
RNHCOOR
RNH_2
CO_2
Poly-carbonates
Poly-urethans
Perennial Energy
Water as H-source
HCs
HCOOH
CO
CH_2O
CH_3OH
CH_4
C_2, C_4, Cn, C-O
MTO, MTP, FUEL Cells
Syngas
Resins
MTBE
TAME
DME
CH_3COOH
Methyl-derivatives:
-amines
-acrylates
-halides
Chemicals
Fuels
CH_2O

From fundamental studies to applications

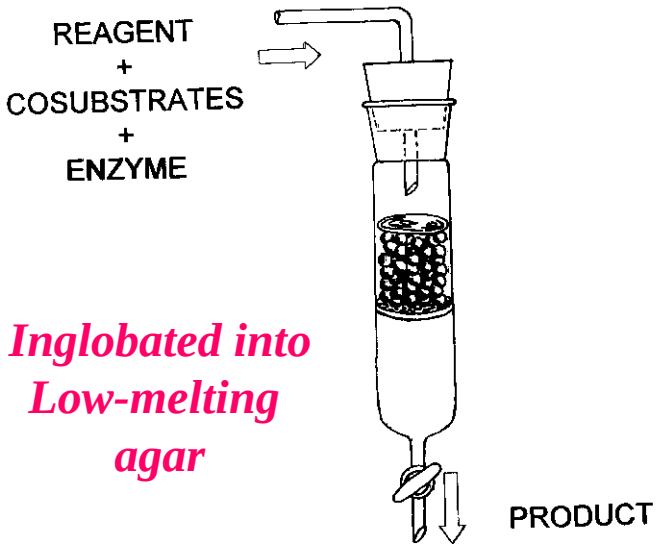


Enzymatic Phenol Carboxylation



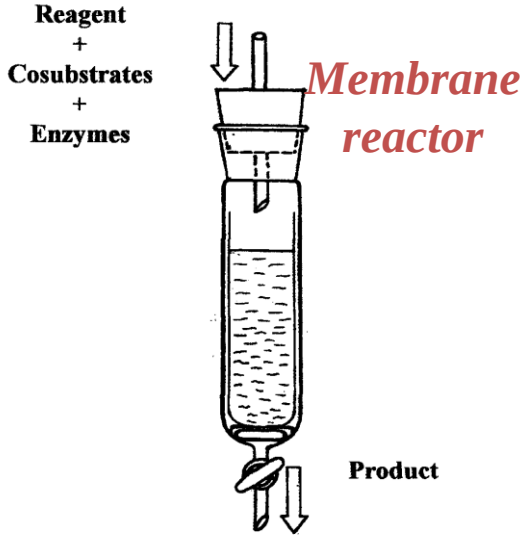
TON = 1600

TOF = 60



Inglobated into Low-melting agar

Aresta, M., Tommasi, I., Dileo, C. *Tetrahedron*, 54(1998), 8841 - 8846



Membrane reactor

Aresta M., Dibenedetto A. *Rev. Mol. Biotech.*, 90, 113-128, 2002

Synthesis $2ROH + CO_2 = (RO)_2CO + H_2O$ and uses of dialkyl carbonates....

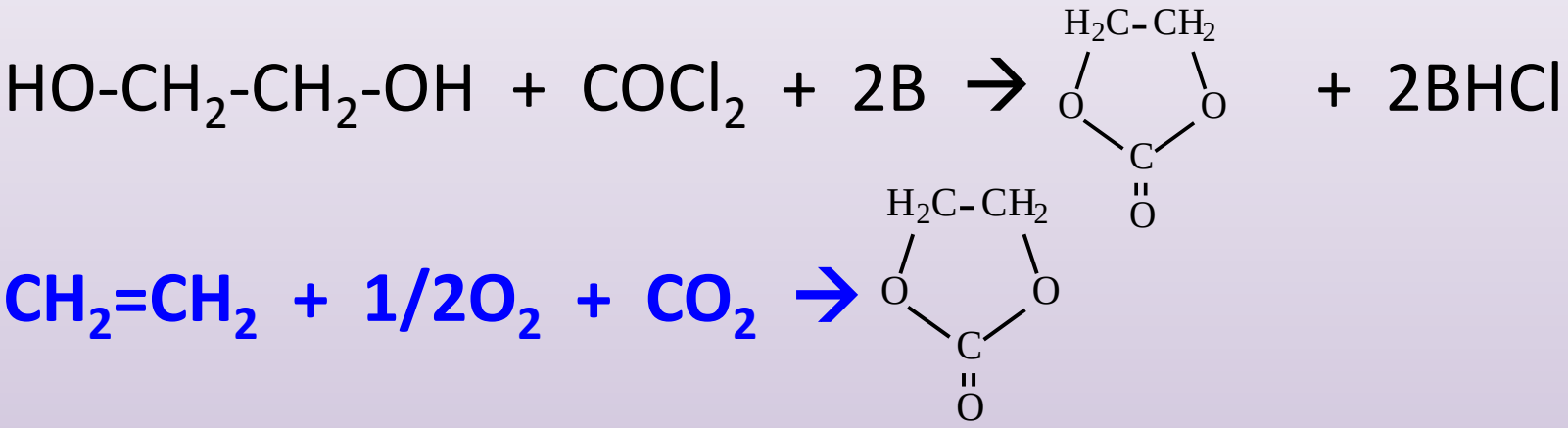
The water issue.

Shifts the Equilibrium

Damages the Catalysts

Membrane Reactors

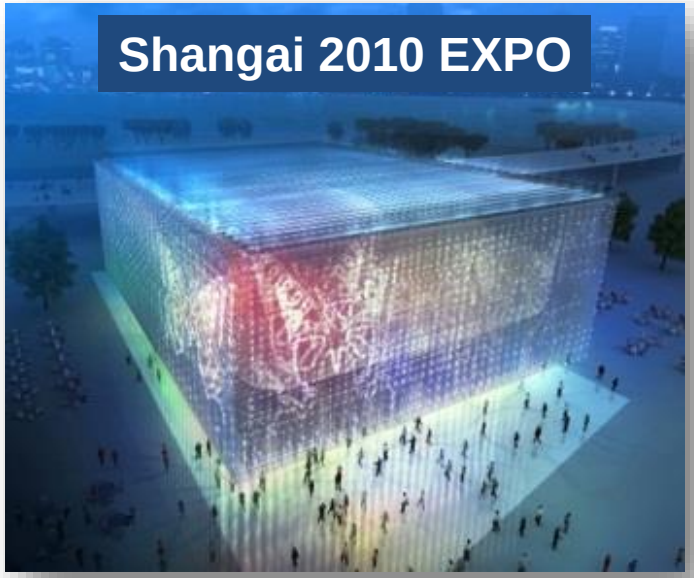
Cyclic carbonates



- ✓ **The oxidative carboxylation would avoid the use of phosgene and the production af waste**.
- ✓ The synthetic methodology based on the use of epoxides and CO_2 finds a limit in the amount of H_2O_2 produced worldwide and is expensive.

Architecture and PCs

Library of the Sung Kyun Kwan University-Seoul



The Barbie House Shangai

Attempts to improve or mimic Nature

- Enhanced photosynthesis
- Man-made photosynthesis
  (Artificial leaf !!? Artificial tree!!?)
- Man-made microorganism……
- Integration of Biotechnologies and Catalysis
- Solar chemistry

Nature. 2014 Sep 25; 513(7519):547-50. doi: 10.1038/nature13776. Epub 2014 Sep 17.

A faster Rubisco with potential to increase photosynthesis in crops

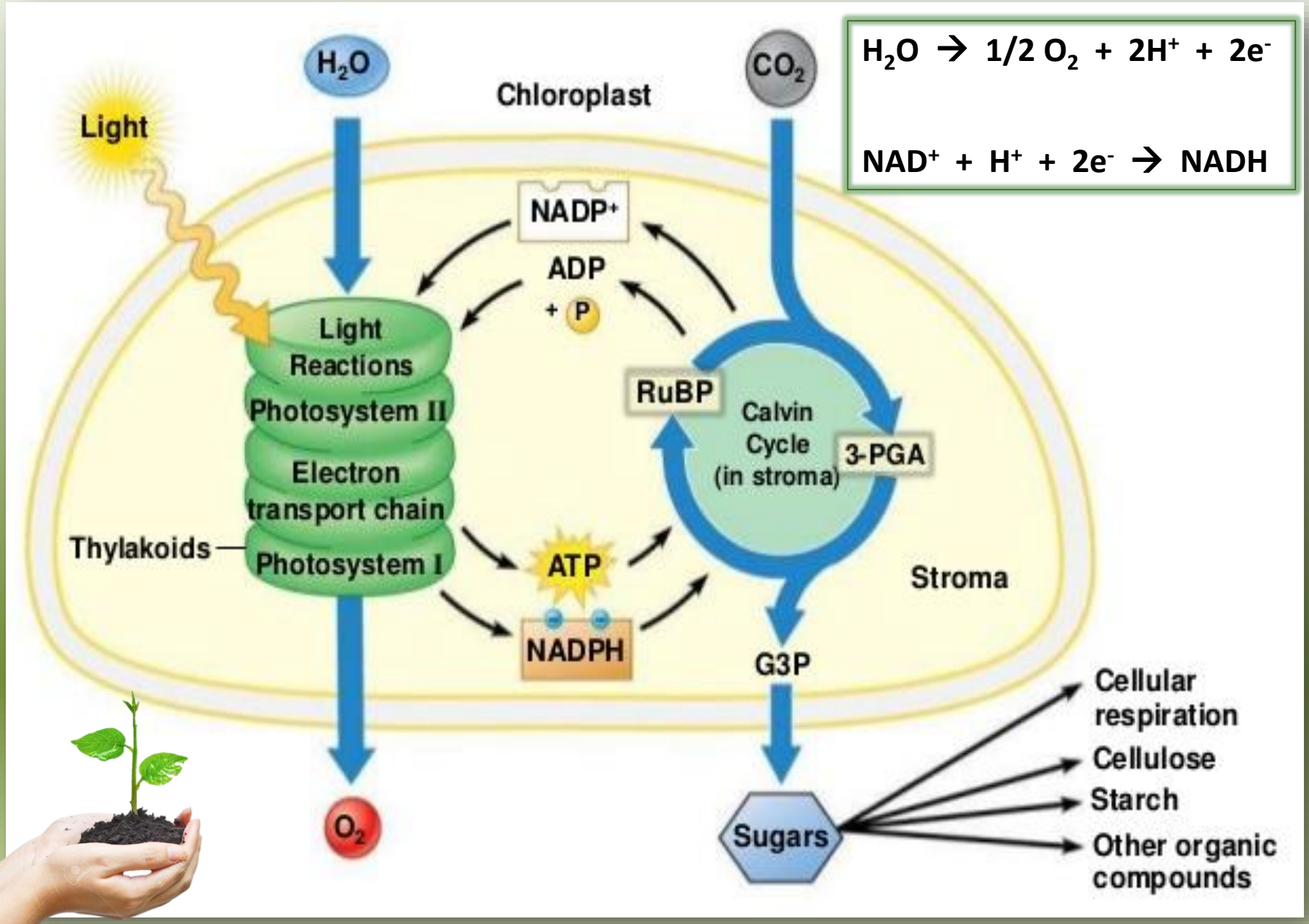
Lin MT[1], Occhialini A Andralojc PJ Parry MA Hanson MR

[1] Department of Molecular Biology and Genetics, Cornell University, Ithaca, New York 14853.
[2] Plant Biology and Crop Science, Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ.
[3] Plant Biology and Crop Science, Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, UK.
[4]Department of Molecular Biology and Genetics, Cornell University, Ithaca, New York 14853.

Abstract

In photosynthetic organisms, D-ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) is the major enzyme assimilating atmospheric CO_2 into the biosphere. Owing to the wasteful oxygenase activity and slow turnover of Rubisco, the enzyme is among the most important targets for improving the photosynthetic efficiency of vascular plants introducing the CO_2-concentrating mechanism (CCM) from cyanobacteria into plants could enhance crop yield. However, the complex nature of Rubisco's assembly has made manipulation of the enzyme extremely challenging, and attempts to replace it in plants with the enzymes from cyanobacteria and red algae have not been successful. Here we report two transplastomic tobacco lines with functional Rubisco from the cyanobacterium *Synechococcus elongatus* PCC7942 (Se7942). These transplastomic tobacco lines represent an important step towards improved photosynthesis in plants and will be valuable hosts for future addition of the remaining components of the cyanobacterial CCM, such as inorganic carbon transporters and the β-carboxysome shell proteins

Basics of photosynthesis

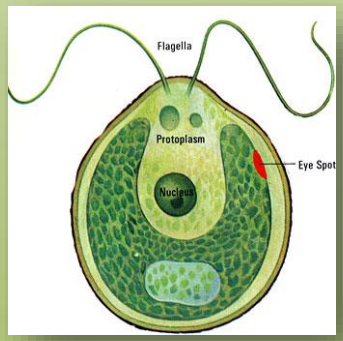


Hydrogen producing microorganisms

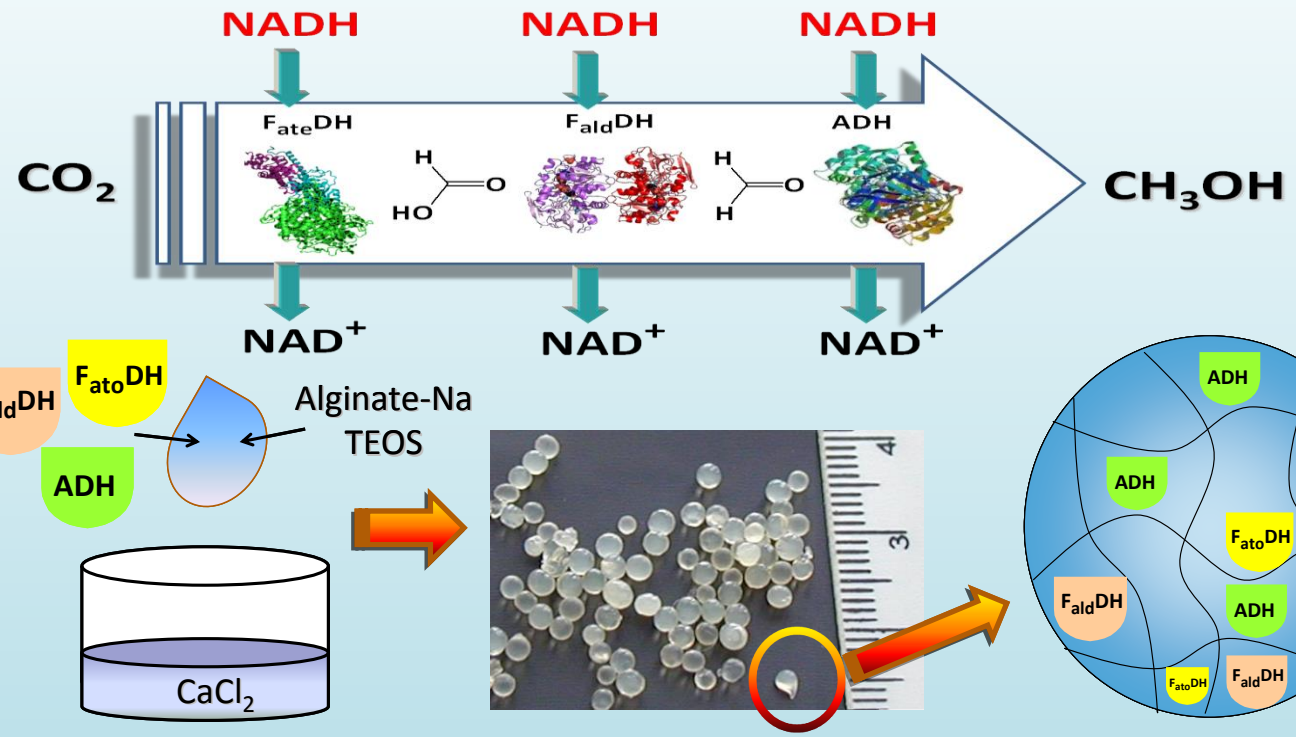
No O_2 evolution!

- Anaerobic digestion → Dark process
  - Acid forming phase → H_2 production (1-8 h)
  - Hydrogenases are required
    - H_2 forming
    - H_2 consuming

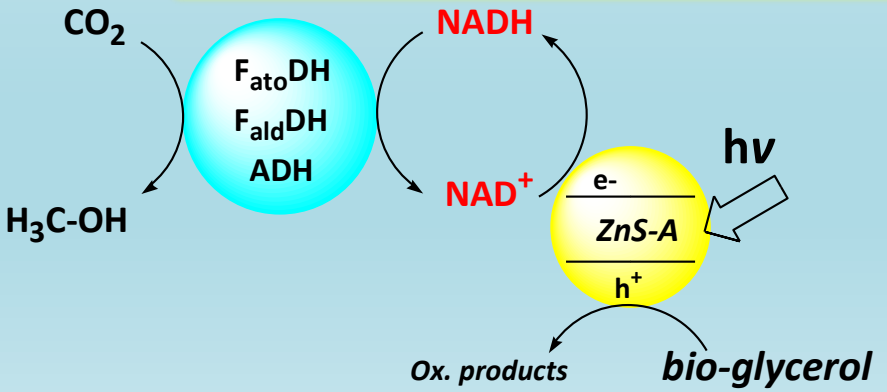
- Photosynthetic microorganisms (anoxygenic)
  - Cyanobacteria Blue-green algae
    - *Clamidomonas*



Hybrid reduction of CO_2

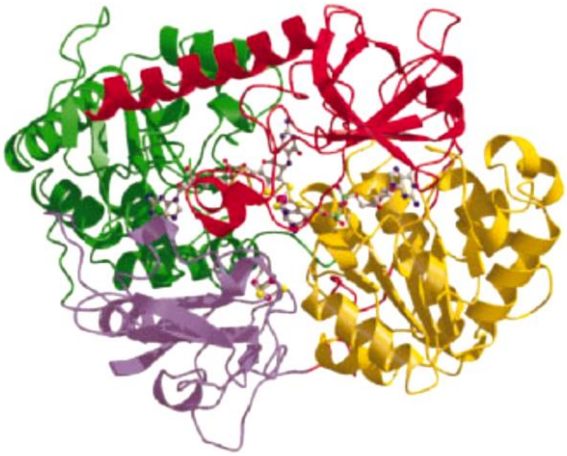


Use of ZnS-A and Ru/ZnS as light harvesting system (Xe)



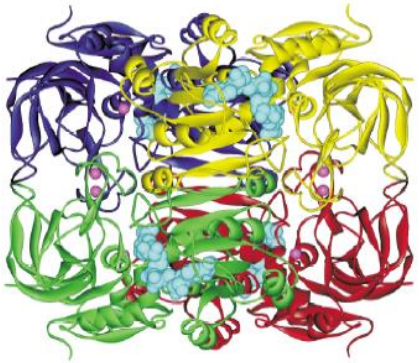
From 3NADH/CH_3OH to >100 CH_3OH/NADH

M. Aresta et al, ChemSusChem, 2012
BJOC, 2015

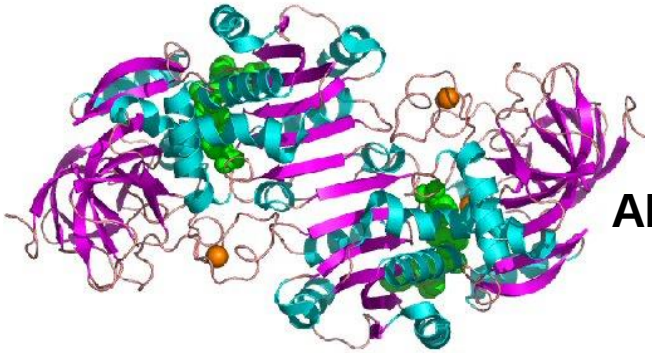


FDH

e-



FAldD

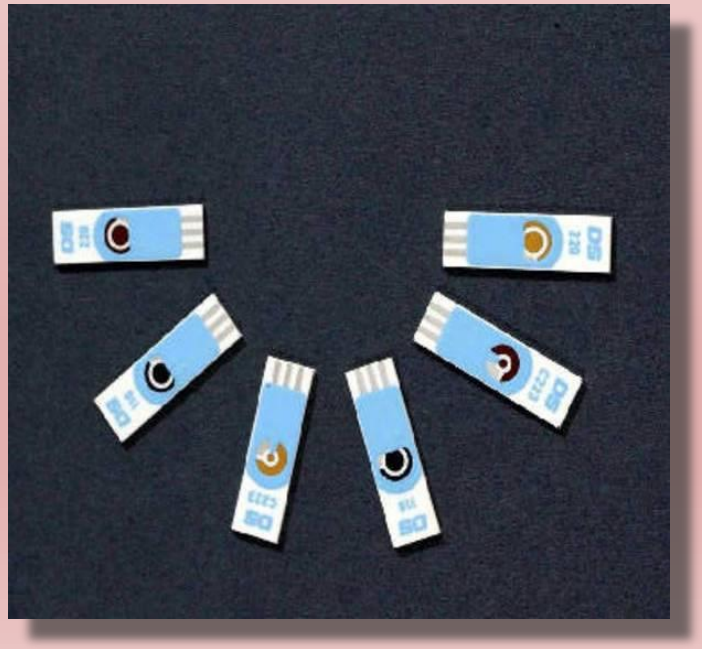


ADH

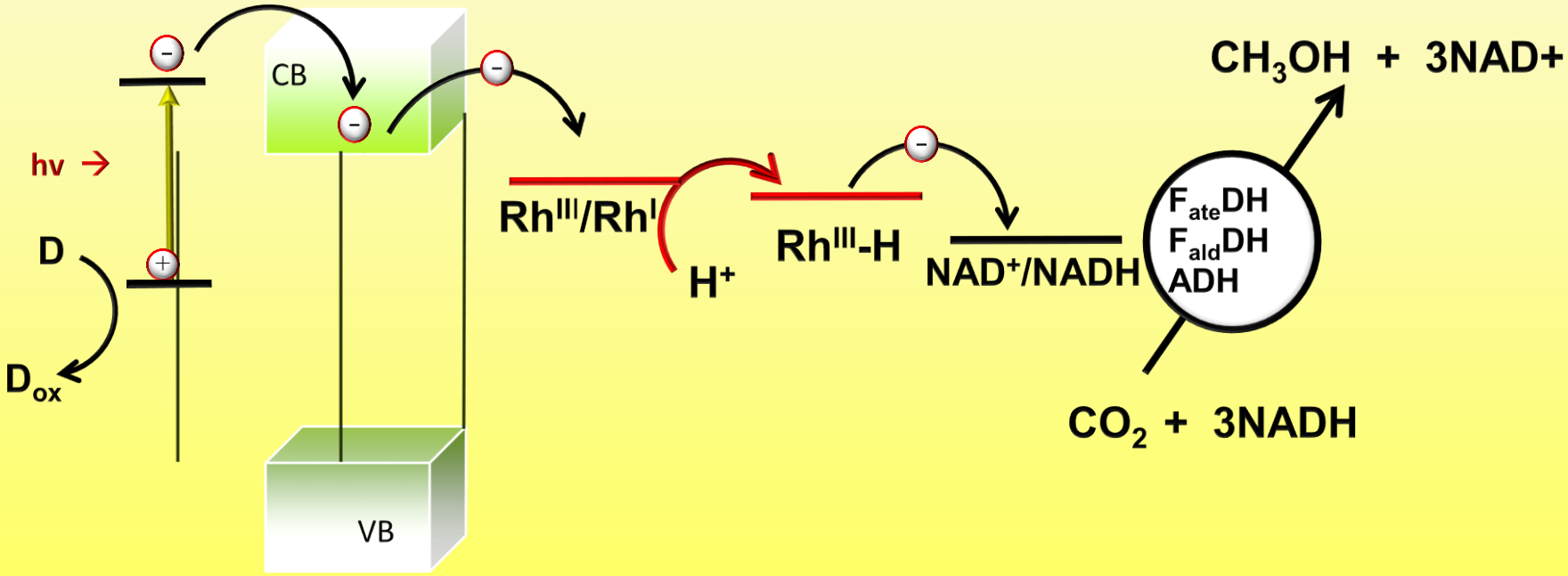
Regeneration of NADH

Enzymes supported on an electrode

PV-e^- injection



Hybrid CO_2 Reduction: Electron cascade in the Vis-Light photochemical regeneration of NADH using modified TiO_2 as solar energy utilizer and a Rh complex as e^- and H^- transfer mediator



From 3NADH/CH_3OH to over 1000 CH_3OH/NADH!

M. Aresta, A. Dibenedetto, T. Baran, W. Macyk, Patent 2015

Fermentation of CO_2 with H_2

Use of bacterial strains able to convert CO_2 and H_2 into :

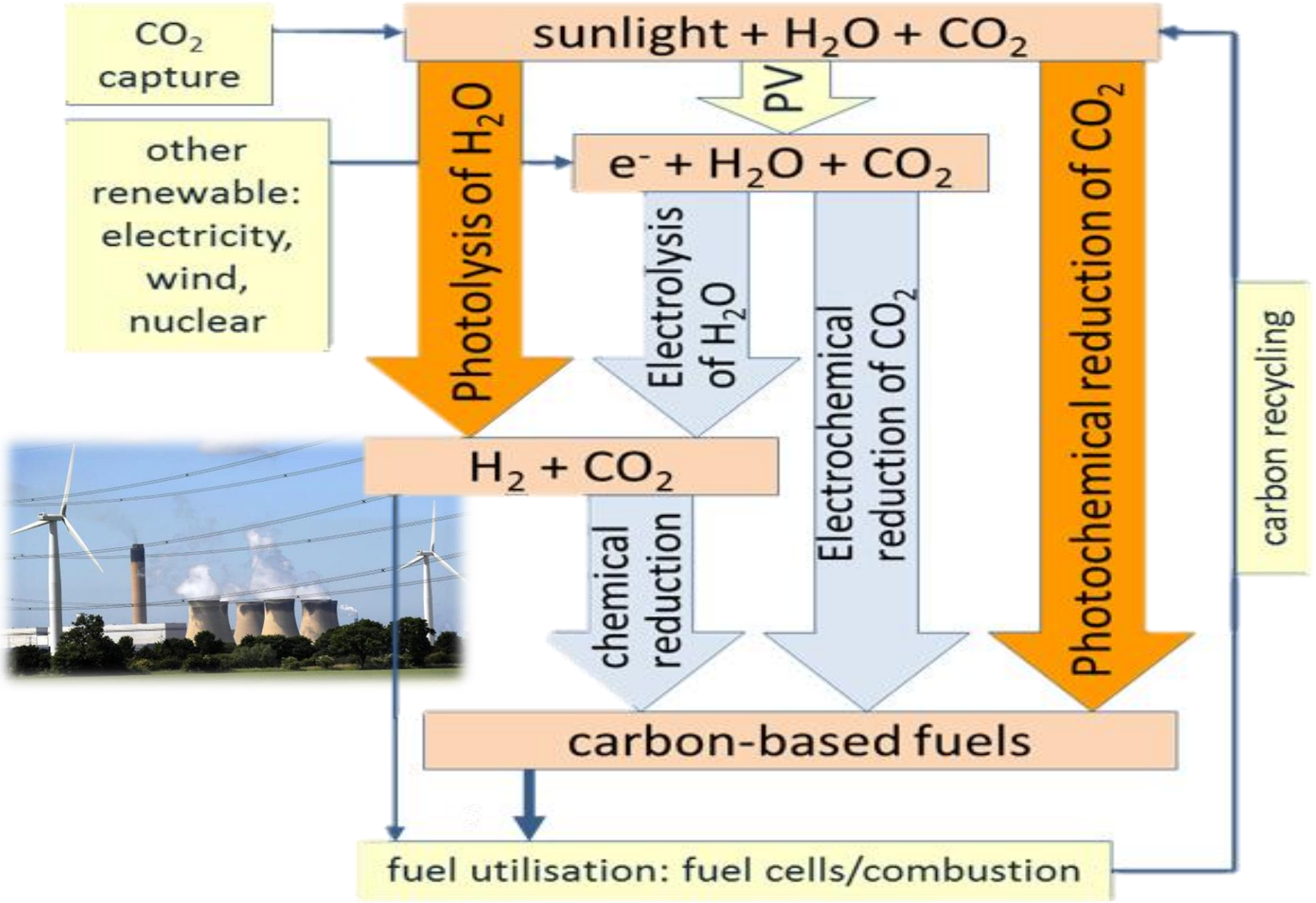
- ✓ **Formate HCO_2^-**
- ✓ **Acetate $CH_3CO_2^-$**
- ✓ **Other Cn**

CO_2

H_2

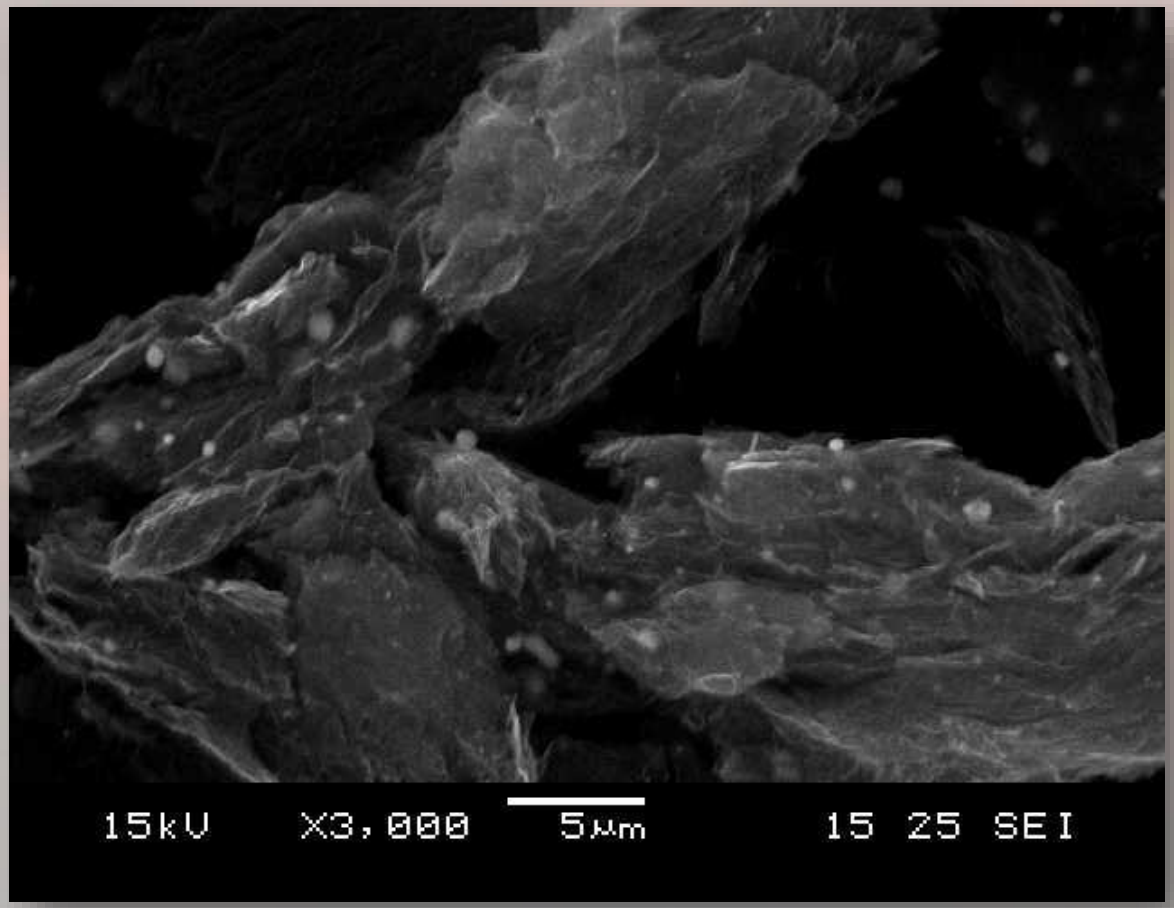
H_2 is produced locally by use of PV

Solar-driven C-recycling



New photocatalytic materials

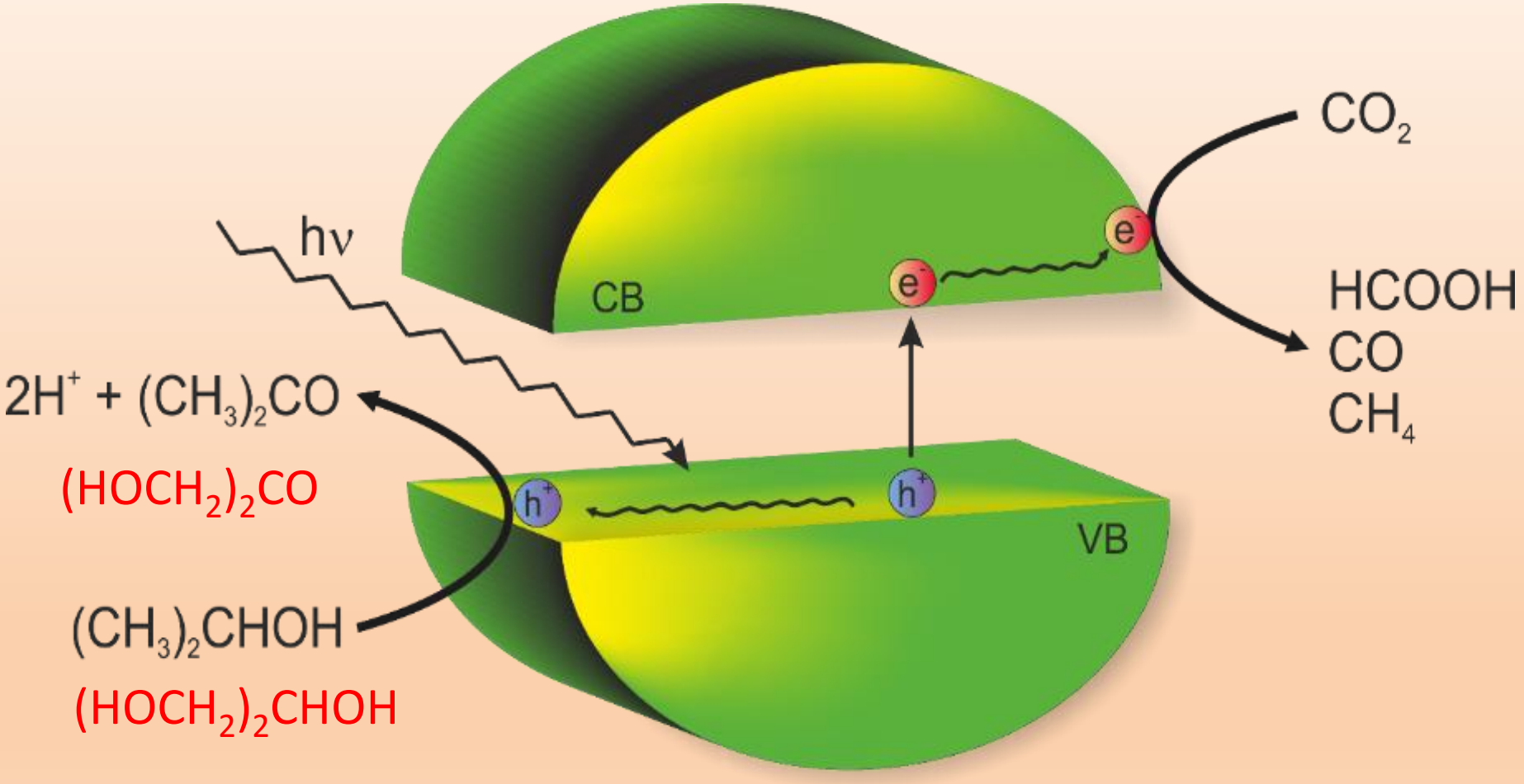
- **Graphene oxide as support for new photocatalysts**



New effective photocatalysts for Carboxylations

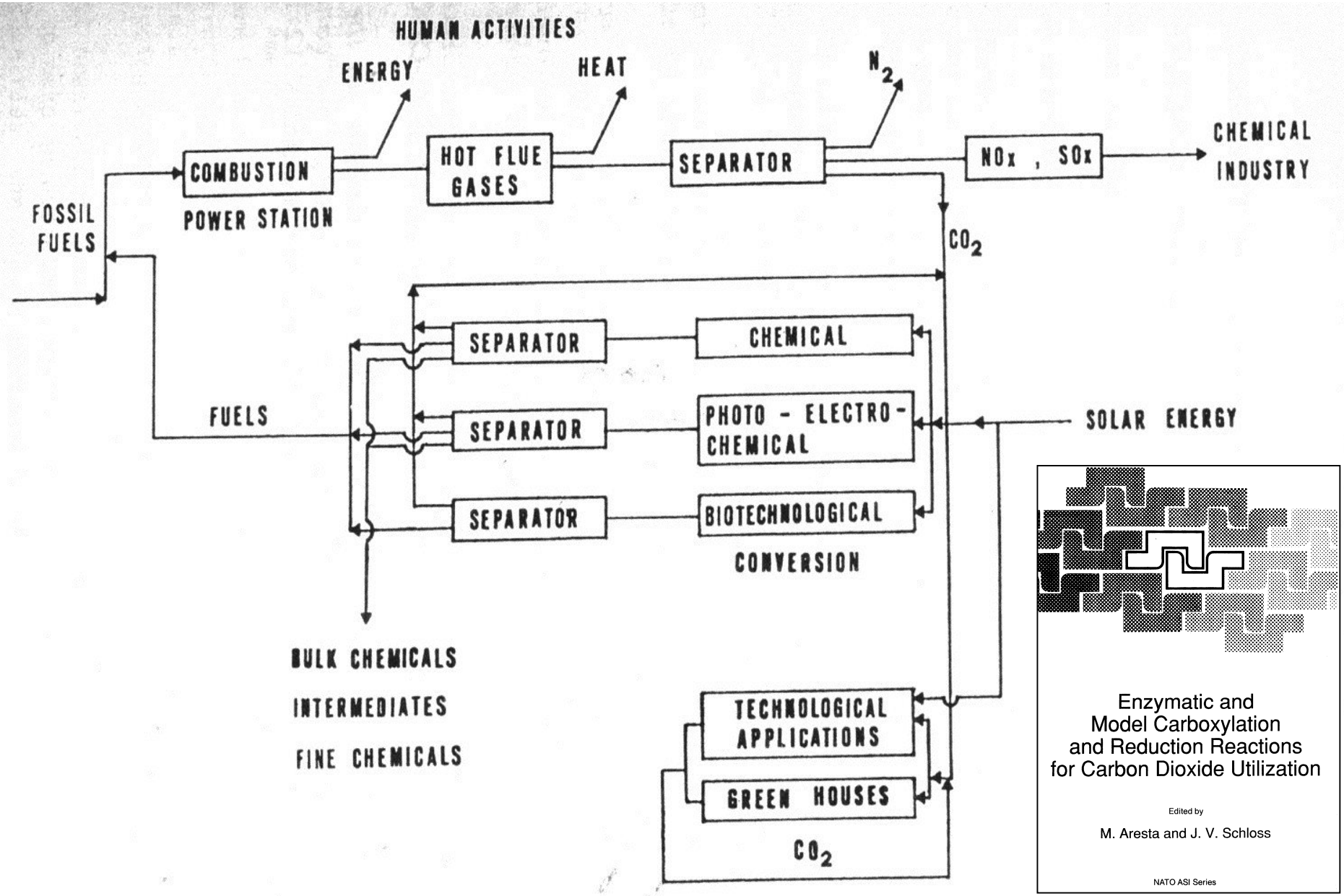
M. Aresta, et al. 2016 submitted

Photoreduction of CO_2 in glycerol (i-propanol) with p-type semiconductors

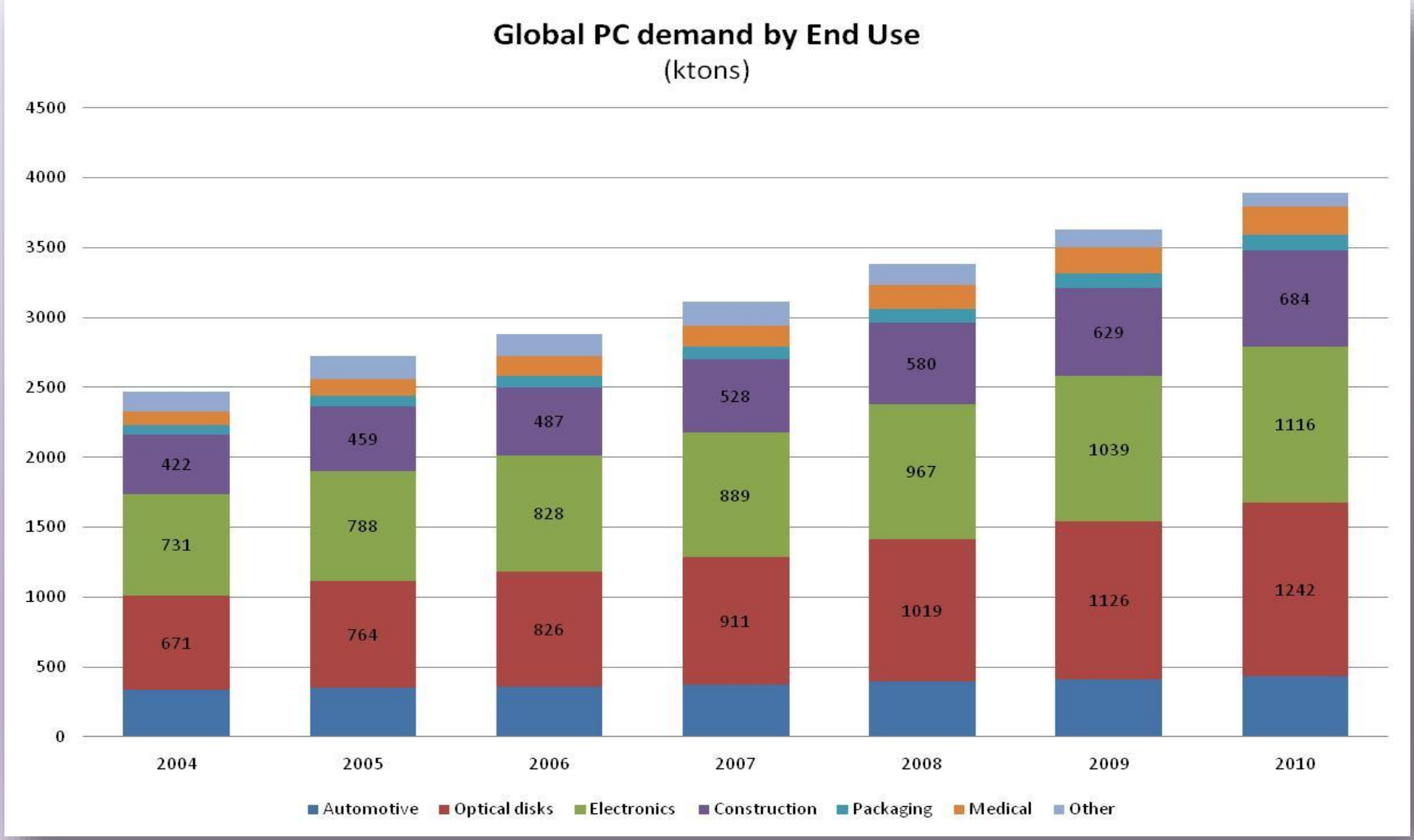


M. Aresta et al, ChemSusChem, 2016

An integrated approach to CO_2 utilization, M. Aresta 1990, NATO ASI Series



Production and uses of PCs



Methanol and DME

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^\circ_{298K} = -49.5$ kJ mol^{-1}

$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O$

$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$

Methanation of CO_2

Sabatier reaction

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H = -165$ kJ/mol

Cn HC and Olefins

$CO_2 + nH_2 \rightarrow C_nH_{2n+2} + RCH{=}CH_2,$

CSP utilization: "Air diesel"

- **Diesel from air**
- **$MO_x \rightarrow MO_{x-1} + 1/2O_2$**

Easy release of "O"

$CeO_2 \rightarrow Ce_2O_3$

Mixed oxides

- **$MO_{x-1} + H_2O \rightarrow MO_x + H_2$**

(> 1000 K)

- **$MO_{x-1} + CO_2 \rightarrow MO_x + CO$**
- **$H_2 + CO \rightarrow FT$**

di-hydroxystearate

hydrolysis

epoxystearate

di-hydroxydation

epoxydation

O_2

C=C cleavage

O_2

pelargonic acid + azelaic acid

metathesis

1-decene + 9-decenoic acid

trans-esterification

esters

biodiesel

epoxydation

O_2

polyepoxide

CO_2

carboxylation

polycarbonate

$H_2N\text{-}R\text{-}NH_2$

amination

urethane-polyol

R= alkyl, aryl

Recent papers and books

Contents lists available at ScienceDirect

Coordination Chemistry Reviews 2016

journal homepage: www.elsevier.com/locate/ccr

Review

My journey in the CO_2-chemistry wonderland

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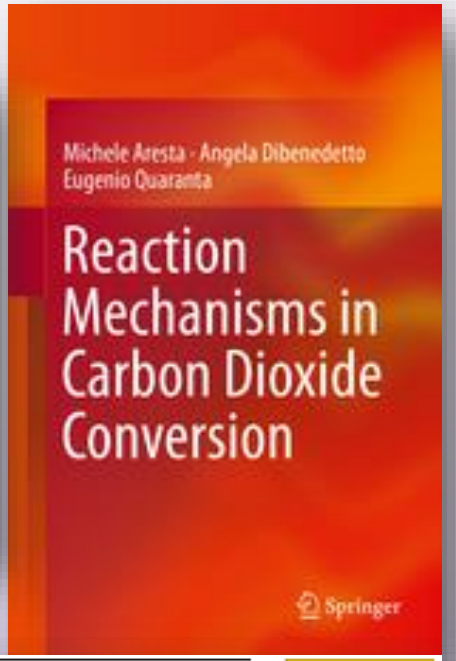
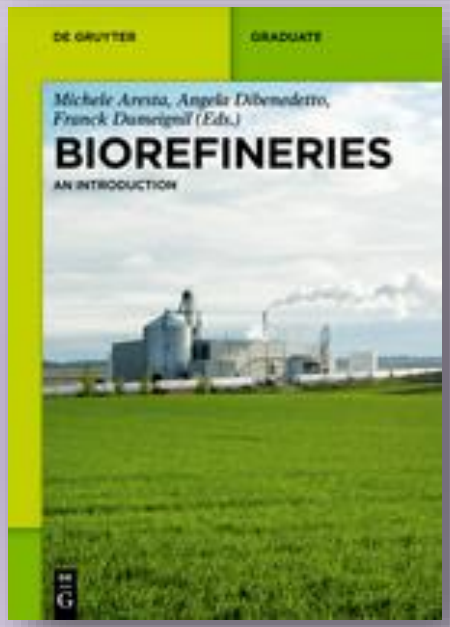
[c] CIRCC, via Celso Ulpiani 27, 70126 Bari, Italy





Contents lists available at ScienceDirect

Journal of Catalysis 2016

journal homepage: www.elsevier.com/locate/jcat

State of the art and perspectives in catalytic processes for CO_2 conversion into chemicals and fuels: The distinctive contribution of chemical catalysis and biotechnology

Michele Aresta [a,b,c,*], Angela Dibenedetto [c,d], Eugenio Quaranta [c,d]

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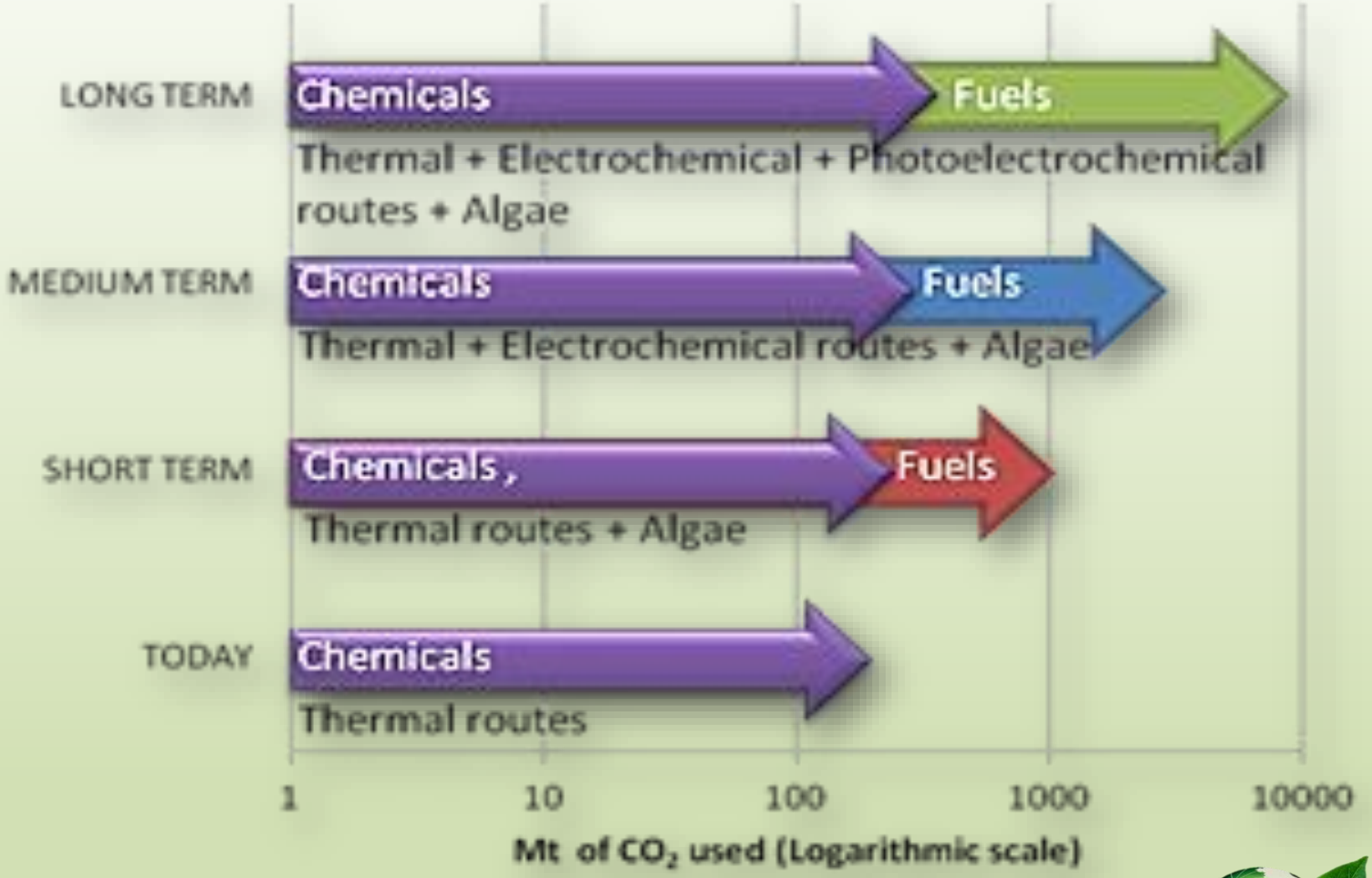
CO_2 utilization is not a dream….. it is reality



Erasmus

“Oh Lord,

Give me twenty more years to live,

The golden age is at hand”

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Catalysis Today 115 (2006) 1

Preface

This issue of *Catalysis Today* is dedicated to Professor Michele Aresta, of the University of Bari, Italy, on the occasion of his 65th birthday, which he celebrated shortly before the opening of the conference. For more than 30 years, since his discovery of a Ni complex of CO_2 (J. Chem. Soc. Chem. Commun. 1975, 636), Professor Aresta has been a passionate proponent of the importance of CO_2 chemistry. He is both the founder and the Permanent Secretary of the International Scientific Committee of the ICCDU conferences. The state-of-the-art chemistry reflected in these pages is a direct result of his tireless energy, boundless enthusiasm, and endless perseverance.

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Catalysis Today 115 (2006) 1
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Preface

Today contains selected Proceedings
nal Conference on Carbon Dioxide
), which was held 20-23 June, 2005,
, Oslo, Norway. The 2005 edition of
vent dedicated to the *chemistry* of
95 participants from 24 different
included 4 Plenary Lectures, 14
ral Contributions, and 53 Poster
ded the topics photo- and electro-
logy of CO_2, separation and storage,
CO_2 and other alternative media, and
homogeneous and heterogeneous catalysis. The scientific breadth of this conference is unique, and the interactions between scientists from the various branches of chemistry lead

exciting areas. Because of this focus on catalysis, the other, non-catalytic topics covered at ICCDU-VIII unfortunately could not be included in this issue. This includes contributions on the enhancement of CO_2 uptake by bacteria, the thermodynamics of CO_2, and modelling studies of CO_2 absorption, among others.

This issue of *Catalysis Today* is dedicated to Professor Michele Aresta, of the University of Bari, Italy, on the occasion of his 65th birthday, which he celebrated shortly before the opening of the conference. For more than 30 years, since his discovery of a Ni complex of CO_2 (J. Chem. Soc. Chem. Commun. 1975, 636), Professor Aresta has been a passionate proponent of the importance of CO_2 chemistry. He is both the founder and the Permanent Secretary of the International Scientific Committee of the ICCDU conferences. The state-of-the-art chemistry reflected in these pages is a direct result of his tireless energy, boundless enthusiasm, and endless perseverance.

Finally, I would like to acknowledge the Norwegian Research Council and the companies Alstom, Hydro, and Statoil for their financial contributions to the conference. I would also like to thank the other members of the Organizing Committee for their hard work before and during the conference. Ultimately, a conference is judged on the quality of the science presented by the attendees. In this aspect I feel ICCDU-VIII was extremely successful, and I would like to thank all the participants, not only for their excellent contributions during the conference, but also their work in submitting papers to these Proceedings and during the peer review of the manuscripts. I would also like to thank my colleagues, especially Drs. Michael Stöcker and Richard Blom, for their encouragement and support in the preparation of this issue of *Catalysis Today*. I hope that the readers find this issue both informative and inspirational.

Guest Editor
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