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Carbon dioxide reduction: perspectives and challenges

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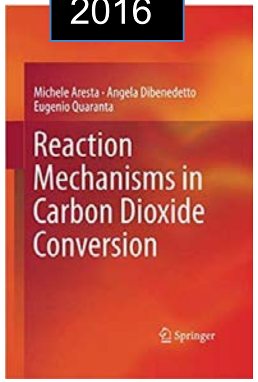
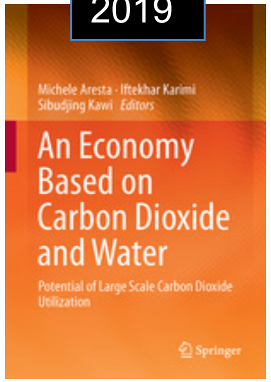
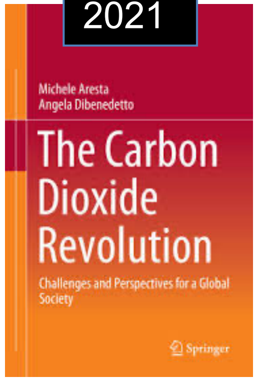
2016



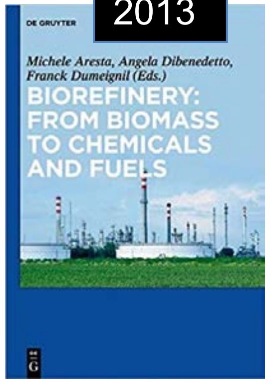
2019



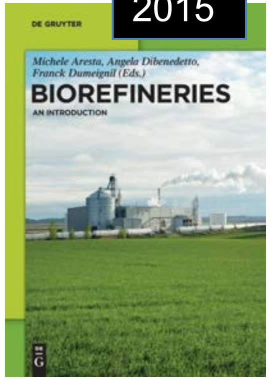
2021



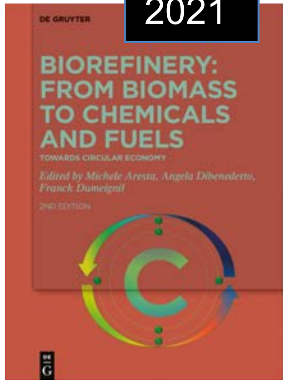
2013



2015



2021



Energy Technology DOI: 10.1002/ente.201600610 **REVIEW**

Biocatalytic and Bioelectrocatalytic Approaches for the Reduction of Carbon Dioxide using Enzymes

Stefanie Schlager,*[a] Angela Dibenedetto,[b] Michele Aresta,[b, c] Dogukan H. Apaydin,[a] Liviu M. Dumitru,[a] Helmut Neugebauer,[a] and Niyazi S. Sariciftci*[a]

Tunable mixed oxides based on CeO_2 for the selective aerobic oxidation of 5-(hydroxymethyl)furfural to FDCA in water†

From the journal: Green Chemistry

Maria Ventura,[a] Francesco Nocito,[b] Elvira de Giglio,[b] Stefania Cometa,[d] Angela Altomare[e] and Angela Dibenedetto *abc

CHEMICAL REVIEWS — 1471 Citations — Review — pubs.acs.org/CR

Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2

Michele Aresta,*† Angela Dibenedetto,†‡ and Antonella Angelini†‡

PERSPECTIVE — www.rsc.org/dalton | Dalton Transactions

Utilisation of CO_2 as a chemical feedstock: opportunities and challenges

Michele Aresta*[a] and Angela Dibenedetto[b]

Received 17th January 2007, Accepted 14th May 2007
First published as an Advance Article on the web 26th June 2007
DOI: 10.1039/b700658f

Journal of Catalysis

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]

Mini-review — SCI

Received: 6 June 2013 Revised: 18 September 2013 Accepted article published: 7 October 2013 Published online in Wiley Online Library: 14 November 2013

Use of carbon dioxide as feedstock for chemicals and fuels: homogeneous and heterogeneous catalysis

Angela Dibenedetto,* Antonella Angelini and Paolo Stufano

ChemSusChem — Chemistry-Sustainability-Energy-Materials

Minireview

The Future of Carbon Dioxide Chemistry

Prof. Angela Dibenedetto, Dr. Francesco Nocito

First published: 15 September 2020 | https://doi.org/10.1002/cssc.202002029

Fuel Processing Technology — Volume 86, Issues 14–15, October 2005, Pages 1679-1693

Utilization of macro-algae for enhanced CO_2 fixation and biofuels production: Development of a computing software for an LCA study

Michele Aresta, Angela Dibenedetto, Grazia Barberio

Current Opinion in Green and Sustainable Chemistry — Volume 21, February 2020, Pages 34-43

Review article

Atmospheric CO_2 mitigation technologies: carbon capture utilization and storage

Francesco Nocito[1], Angela Dibenedetto[1,2]

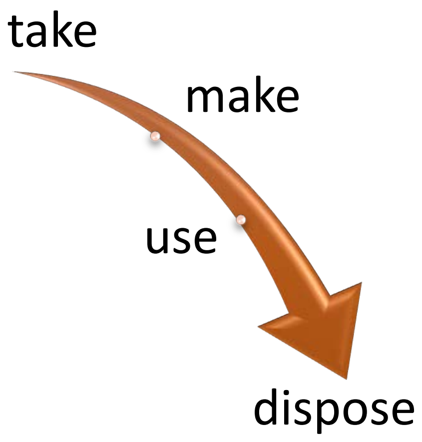
Introduction

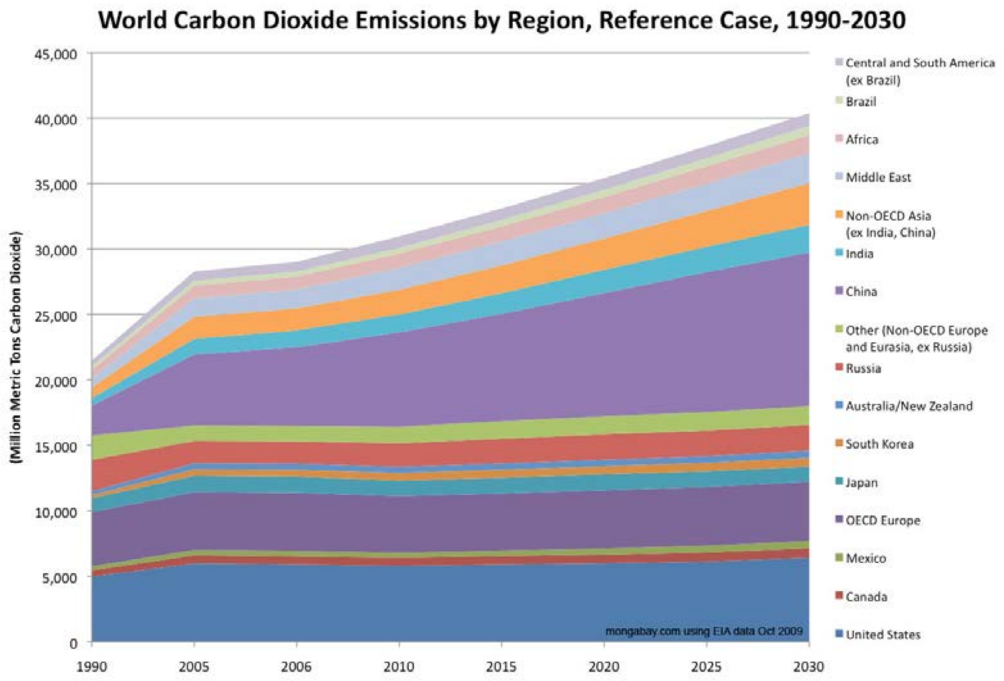
- *Linear C-economy: the effects*
- Technologies for the conversion of large volumes of *spent-carbon* into *working-carbon*
  - *Direct conversion of CO_2 vs Utilization of biomass*
- *Man-made photosynthetic processes*
  - *Photochemical CO_2 conversion*
- *Integration of catalysis and biotechnology*
- *Oily biomass (microalgae)*
- *Cellulosic biomass*
- *Circular C-economy:* ***our future***

transition

Chem Rev 2014

Society and CO_2





CO_2 capture

The capture of CO_2 from continuous and concentrated point sources such as power plants (at a cost of 30-130 US$/t) or industry (at a cost depending on the purity of the source) or directly from the atmosphere (at cost of 180-300+ €/t, due to the low concentration), may contribute to reduce its accumulation in the atmosphere.

CCS option

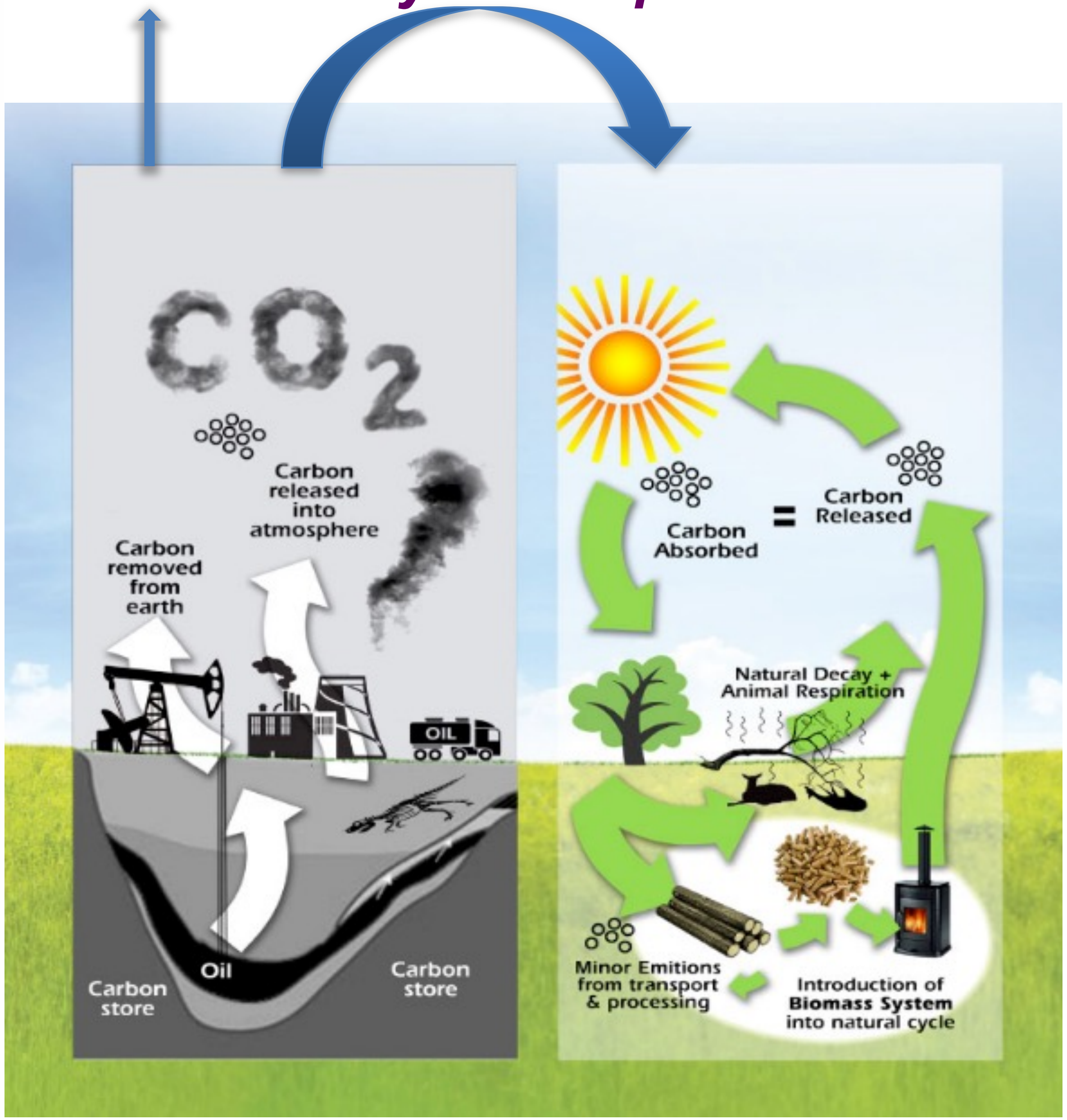
Disposal in natural fields

CCU option

Used for several purposes

M. Aresta, A. Dibenedetto, The Carbon Dioxide Revolution, Springer, **2021**;
F. Nocito, A. Dibenedetto, *Current Op Green & Sust Chem* **2020.**

CCU: *way to complement the natural C-Cycle*



From the linear to the circular C-economy

Use of renewable carbon: our future

Is atmospheric CO_2 a renewable-C?

- **In a circular economy view, CO_2 is increasingly considered by the chemical industry as a building block or a source of carbon, rather than a waste.**
- **In some cases, the use of CO_2 for the production of chemicals is already at the commercial level.**

Circular Economy Lab

- Efforts are underway to react CO_2 with olefins, dienes, alkynes, alcohols, amines, epoxides etc to form carboxylates, carbonates and carbamates. Many of such processes are catalytic.
- Some processes are endergonic and thus more difficult to implement.

The Alternatives, the Challenges

- **Direct conversion of Carbon Dioxide:**

  Carbon Dioxide Capture and Utilization-CCU

- **Let Nature to fix CO_2 and use Chemistry to convert biomass into chemicals, materials and fuels**

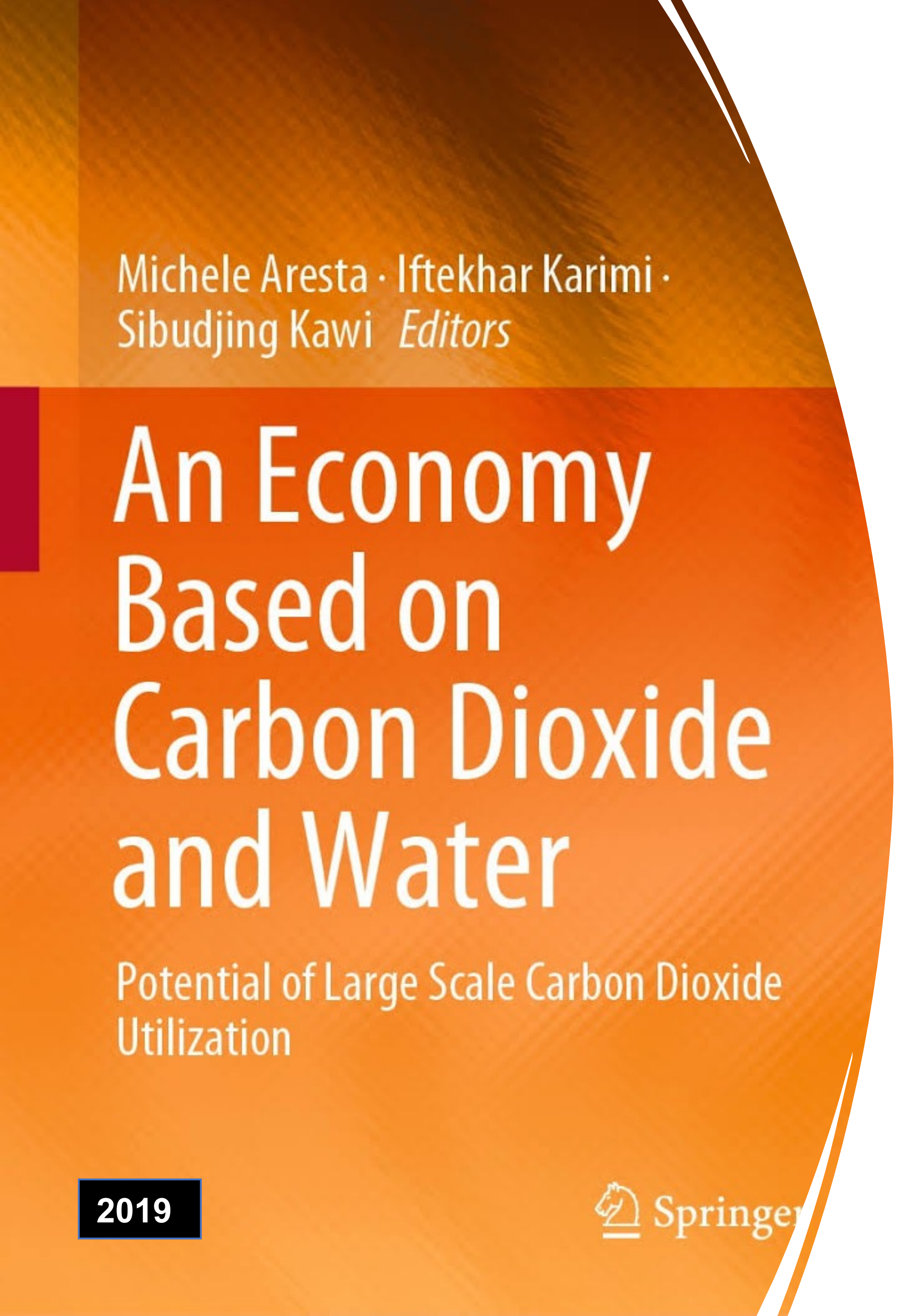
- **Integration of Chemistry and Biotechnology**

Transition from HCH to HCOH

CO CO_2

New Catalysis **New Catalysts**

M. Aresta, A. Dibenedetto, The Carbon Dioxide Revolution, Springer, **2021**

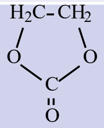


CCU: benefits and challenges

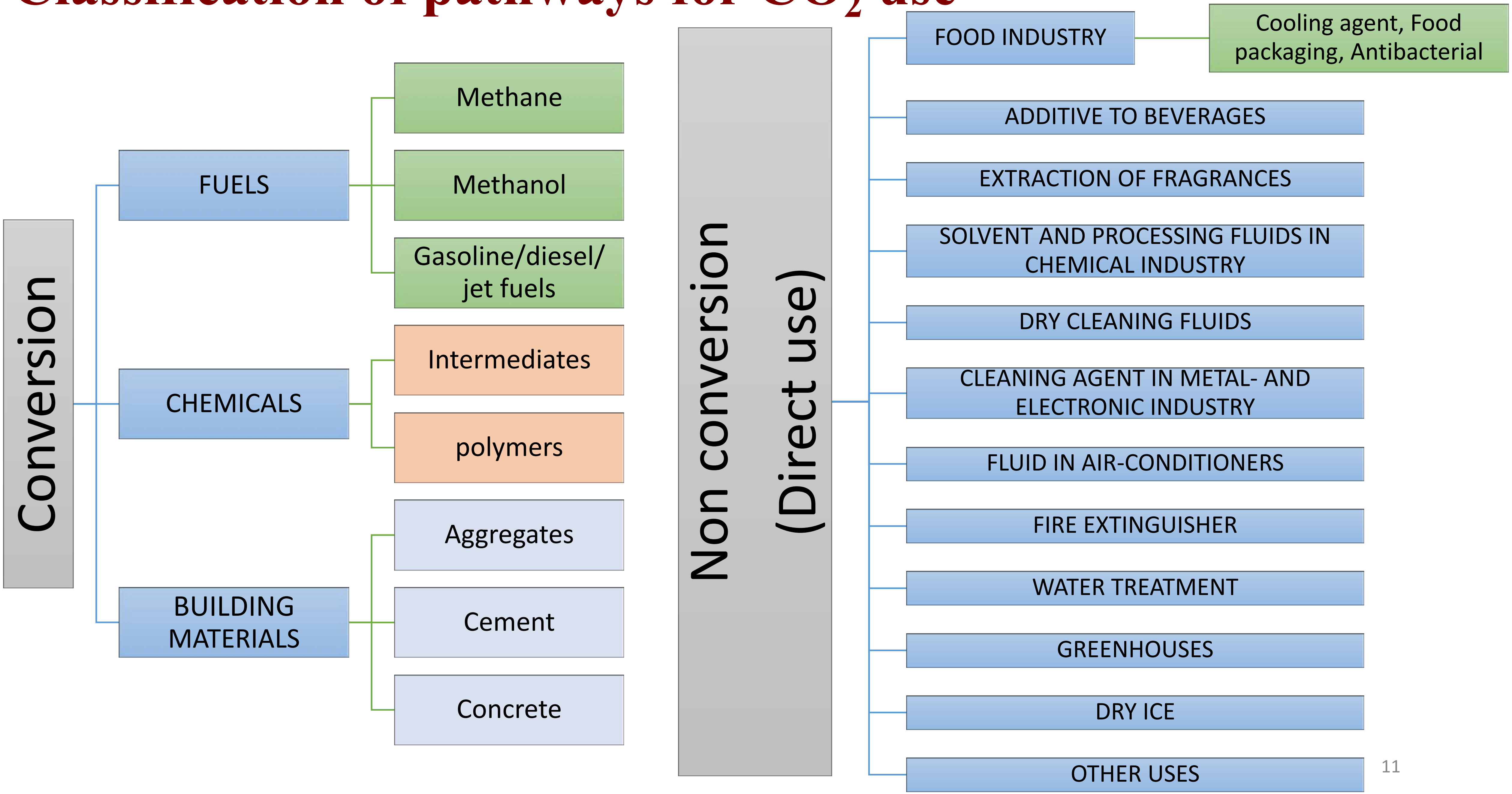
- Affords added value products from a «waste»
  - Fine chemicals, bulk chemicals, materials, fuels
- Reduces fossil fuels extraction and dependence on natural reserves of carbon
- Reduces the CO_2 immission into the atmosphere
- Makes use of perennial energy sources for CO_2 valorisation, mimicking Nature
- May contribute to develop a

CO_2/H_2O-economy

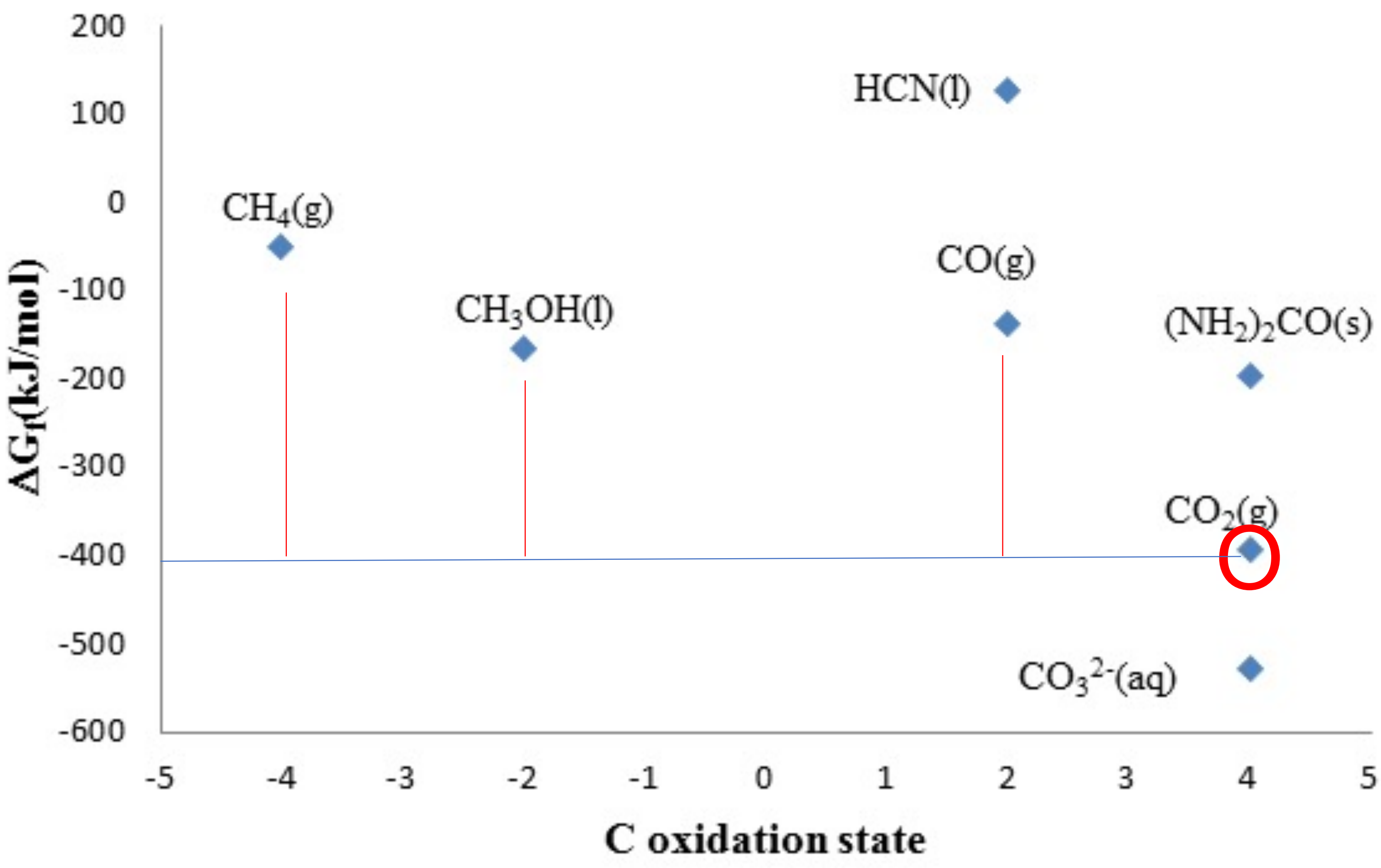
Perspective use of CO_2 to Chemicals

Compound	Formula $C_{oxstate}$	Actual Market Mt/y	CO_2 Use Mt/y	Market 2030 Mt/y	CO_2 use Mt/y
Urea	$(H_2N)_2CO$ +4	180	132	210	154
Carbonates linear	$OC(OR)_2$ +4	>2	0.5	10	5
Carbonates cyclic	 +4				
Polycarbonates	$-[OC(O)OCH_2CHR]-n$ +4	5	1	9-10	2-3
Carbamates	RHN-COOR +4	>6	1	11	*ca.* 4
Acrylates	$CH_2=CHCOOH$ +3	5	(0.5) ?	8	5
Formic acid	HCO_2H +2	1	(0.9) ?	>10	>9
Inorganic carbonates	M_2CO_3 +4 $M'CO_3$	$CaCO_3$ 250	70	400	100
Methanol	CH_3OH -2	60	10	120	>100
Total			207		>370

Classification of pathways for CO_2 use

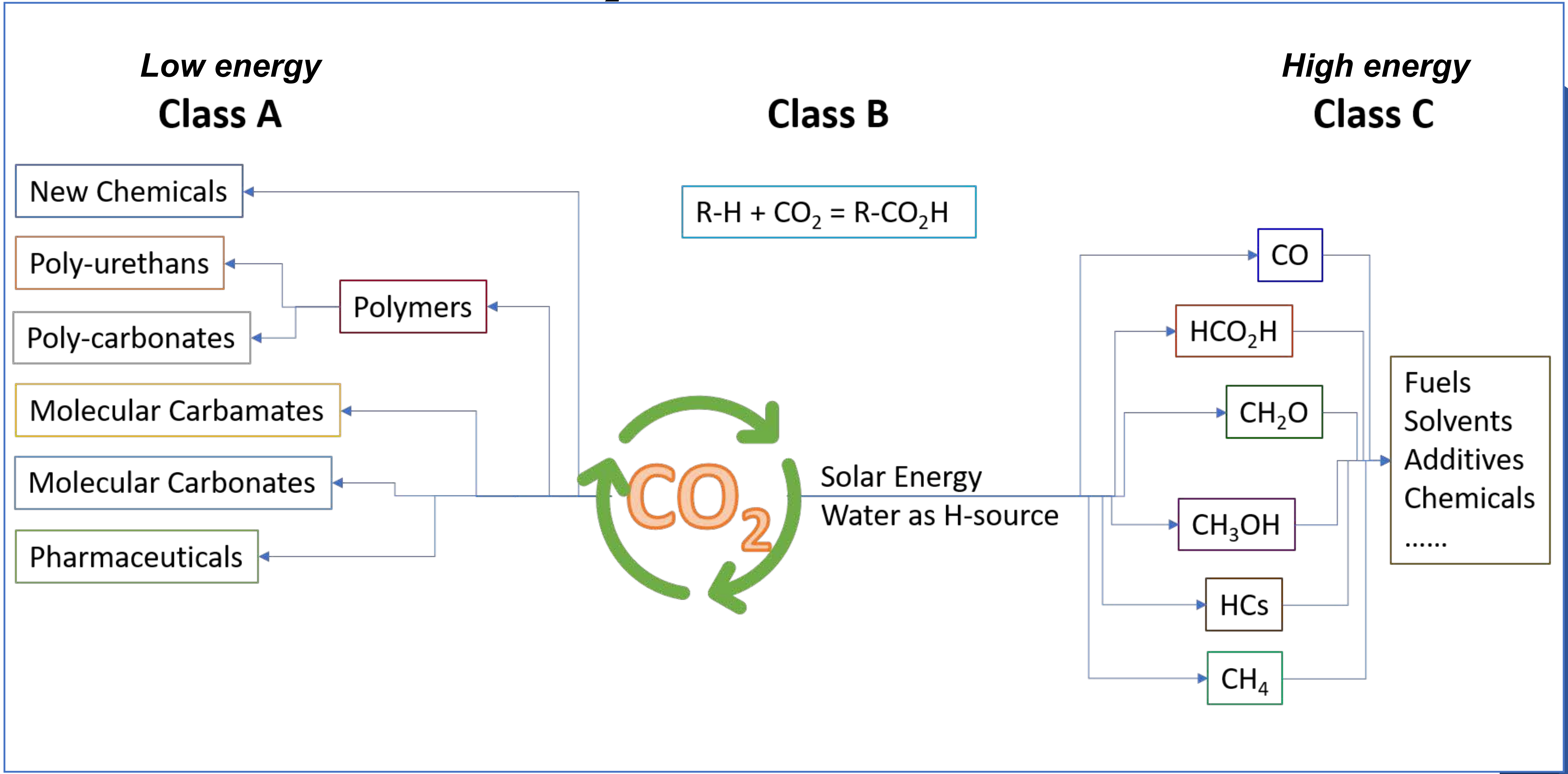


Gibbs standard free-energy



A. Dibenedetto, M. Aresta, A. Angelini *Chem Rev* **2014**

Classes of reactions for CO_2 conversion



A. Dibenedetto, F. Nocito, The Future of Carbon Dioxide Chemistry, *ChemSusChem* **2020**, *13*, 6219–6228

Sources of CO_2 (Except Power stations)

Variable CO_2 Concentration

Industrial Sector	***Mt_{CO2}/y produced***
Oil Refineries	**850-900**
Ethene and other Petrochemical Processes	**155-300**
LNG Sweetening	**25-30**
Ethene oxide	**10-15**
Ammonia	**160**
Fermentation	**>200**
Iron and steel	***ca.* 900**
Cement	**> 1000**

3300-3500

1040-1245

***ca.* 2260**

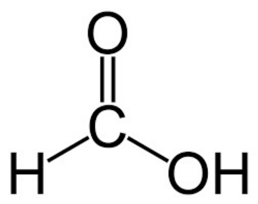
Key Performance Indicators

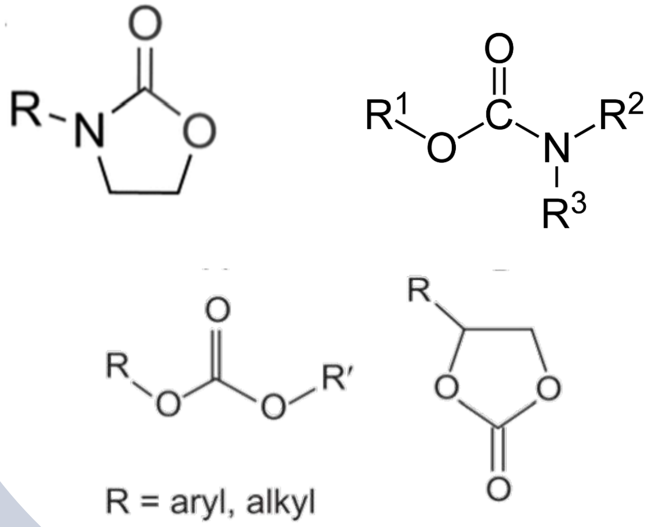
- **E-Factor: Waste produced per unit of product, w/w.** *Fuels: 1-3; Chemicals: 5-100 (from fossil-C)*
- **CF: Carbon footprint -** the CO_2 emission in the process per unit of product: this cannot be used as only criterion;
- **ECF: Energy consumption ratio (E_{out}/E_{in}) -** ratio of the input- to output-energy;
- **CFU: Carbon fraction utilization -** the percentage of reagent-C fixed into the products;
- **A/U: The "avoided" to "used" ratio -** For several applications the ratio avoided CO_2/used CO_2 is in the range 2-5, with a good average around 3.5.

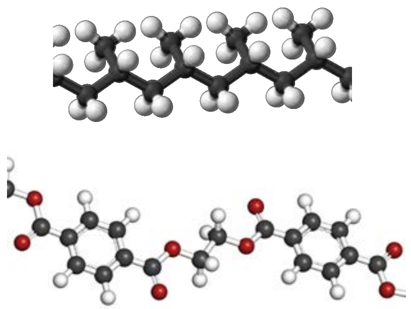
Sustainable Chemical and Polymer Industry

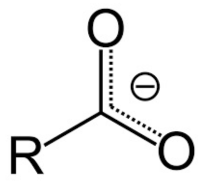
Bulk chemicals

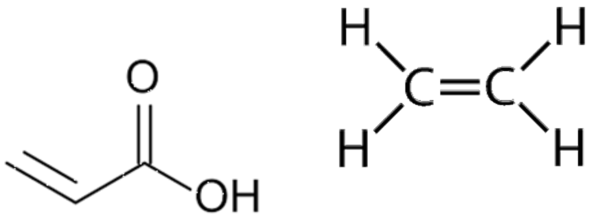
- Carbonates: linear and cyclic
- Carbamates: linear and cyclic
- Formic acid
- Acrylic acid and Acrylates
- Olefins
- Alcohols (C1→Cn) and ethers (DME)
- Carboxylates
- Monomers, Polymers

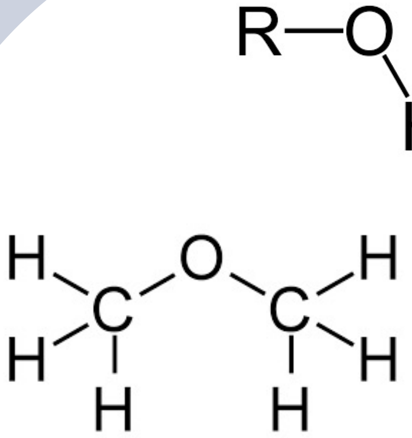






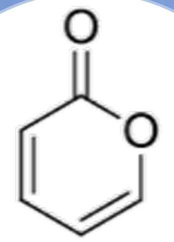




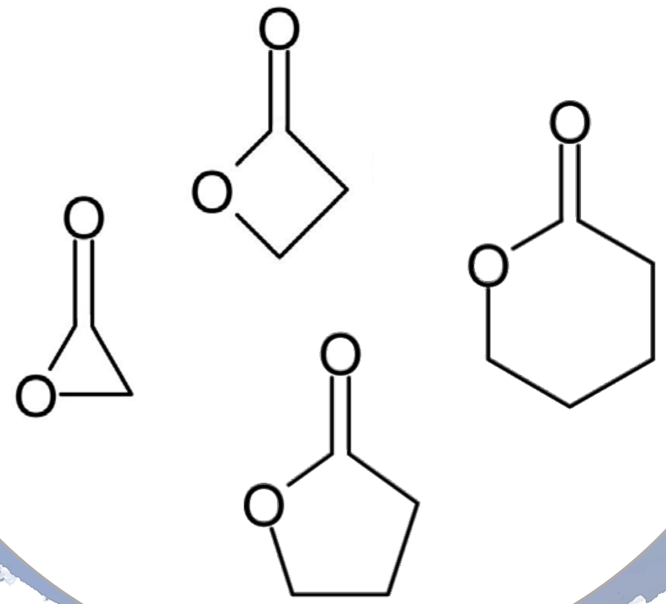


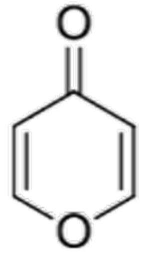
Sustainable Chemical and Polymer Industry

- **Fine chemicals**
  - Lactones
  - Pyrones
  - Pharmaceuticals (direct carboxylation of substrates to afford acids or esters)



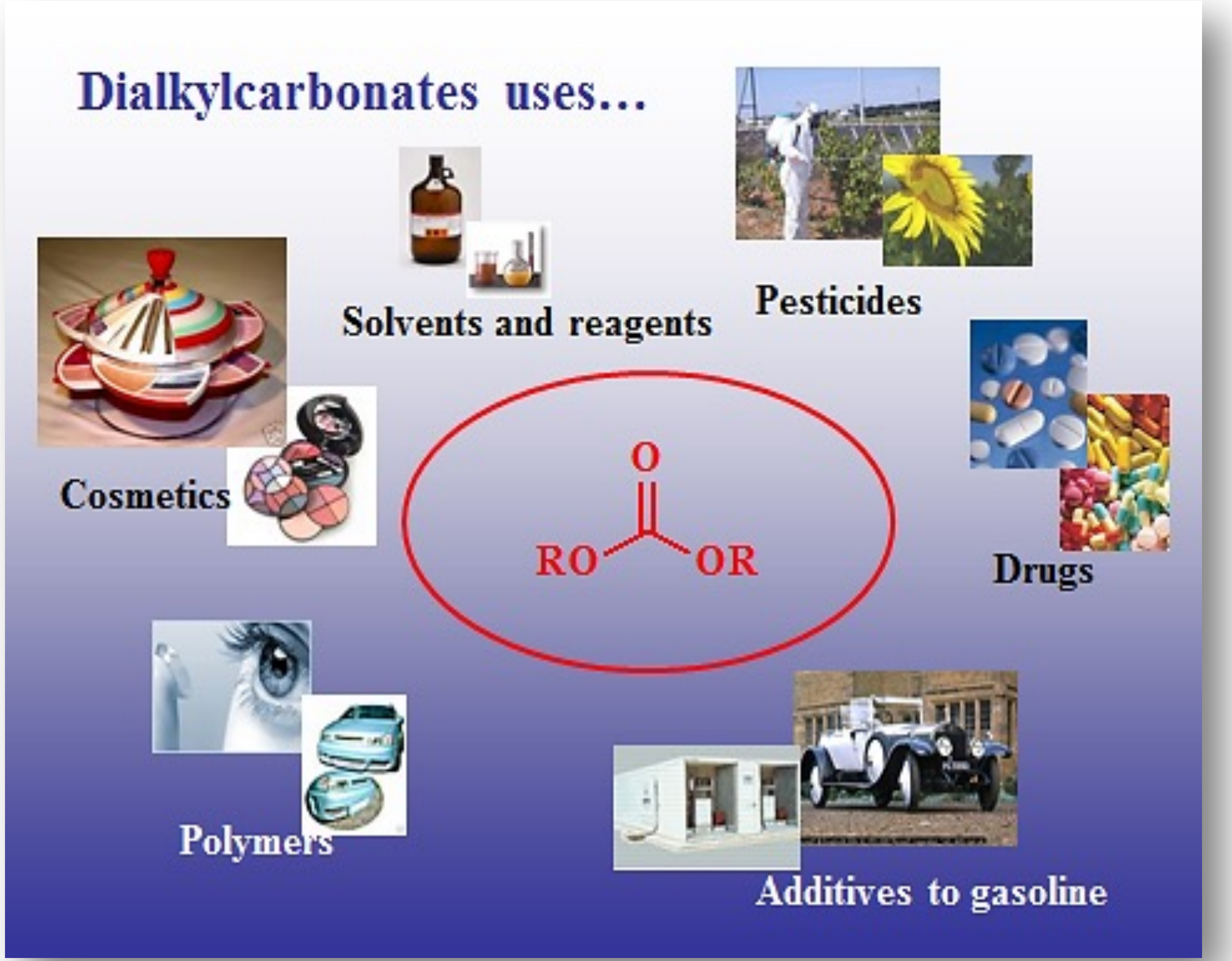
α-Pyrone





γ-Pyrone

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



Linear: Monomers, Reagents, Solvents, Fuels.
Captive use 0.2 Mt > 50 Mt+

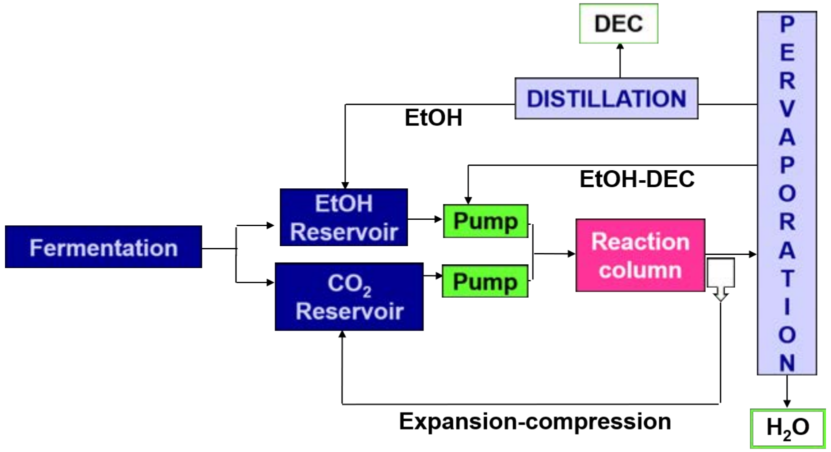
Cyclic: Solvents, Reagents, (Co)-monomers.
Captive use >Mt

Shifts the Equilibrium, Damages the Catalysts

SOLUTIONS

Inorganic Organic Traps, Membrane Reactors, Use of pervaporation membranes

Carbonates: Linear



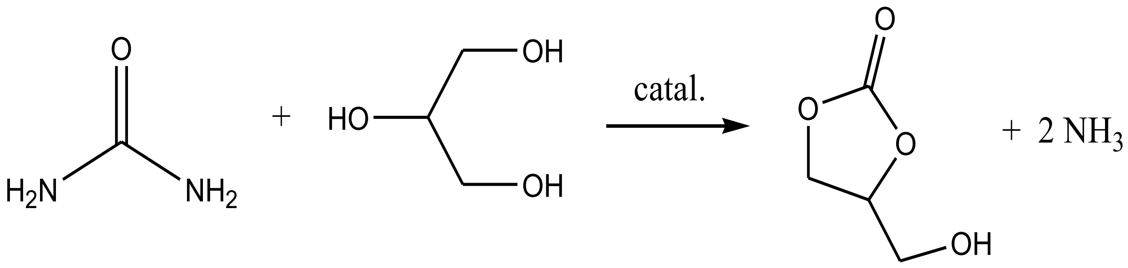
Low energy option, New concept reactor

Aresta, Dibenedetto et al 2012, 2016, 2017, in preparation

Use of Urea, H_2NCONH_2, as active form of CO_2

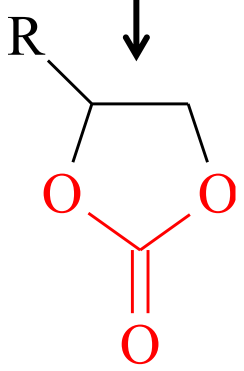
$$CO_2 + 2\ NH_3 \downarrow H_2NCONH_2 + H_2O$$

+ 31 kcal/mol



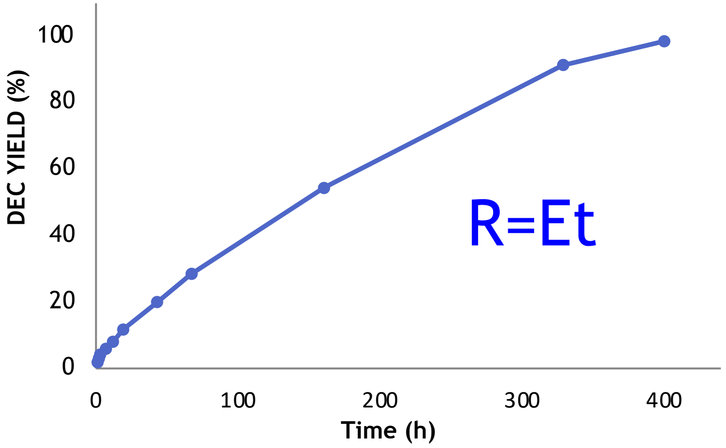
Dibenedetto et al, EU Patent 2010 to Arkema

$$HO\text{-}CHR\text{-}CH_2\text{-}OH + H_2NCONH_2 \downarrow$$



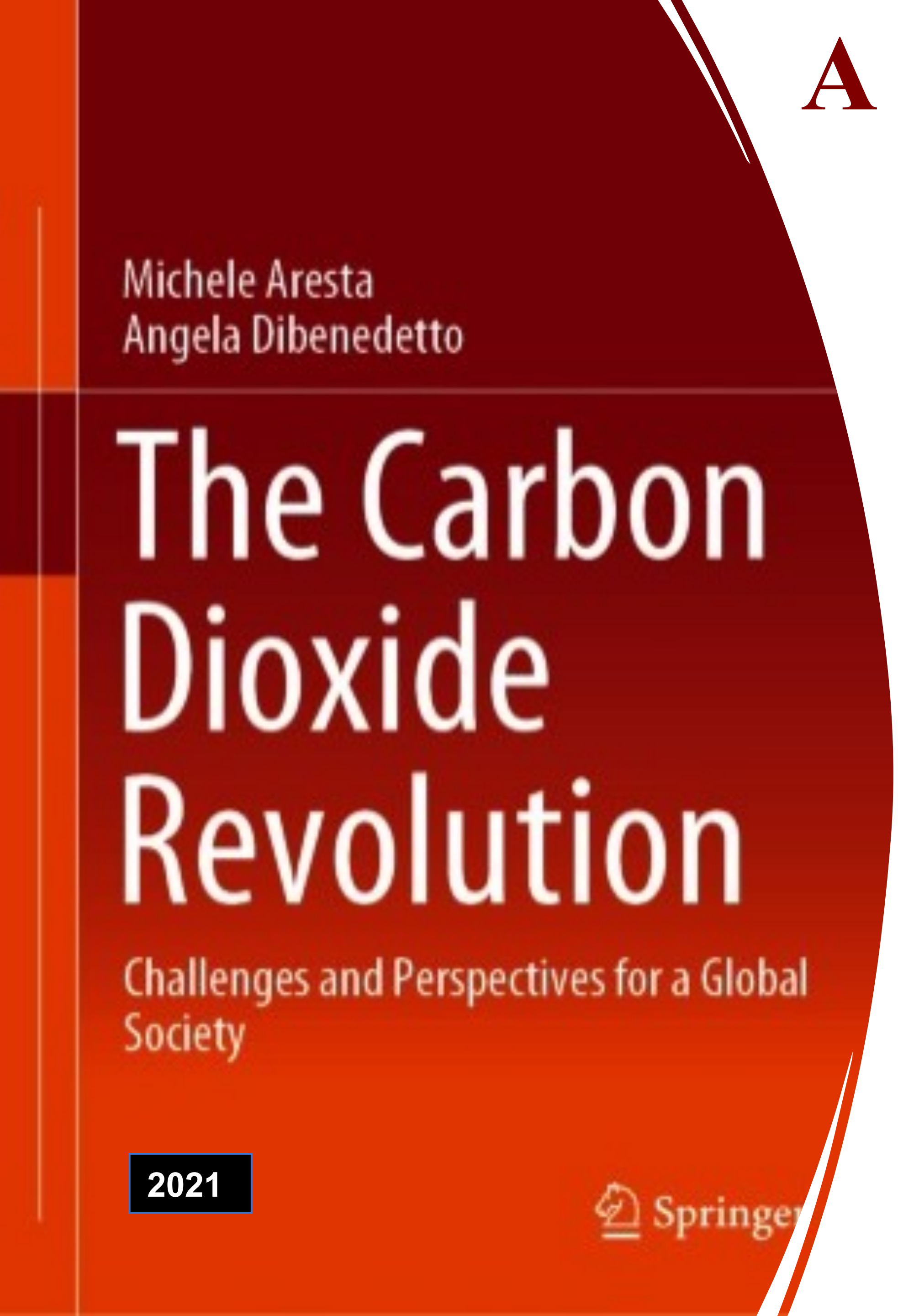
5-6 membered rings.
Dibenedetto et al, Eurobioref Project

$$2ROH + H_2NCONH_2 \longrightarrow ROC(O)OR + 2NH_3$$



better thermodynamics, higher conversion as the reaction is not equilibrium driven

A. Dibenedetto et al, RSC Adv 2015



A new scenario opens

- Change of paradigm in energy supply
- Primary energy sources, intensive utilization and at affordable costs
  - Sun
  - Wind
  - **Storage of solar and wind energy into chemical bonds**
- High energy processes for CO_2 reduction are now feasible with the use of non-fossil carbon based energy sources: such use is close to be cost-effective
- Chemists have to take this opportunity

Dark Chemistry

Chemicals

Use of Low-entropy CO_2

Light Chemistry

Fuels

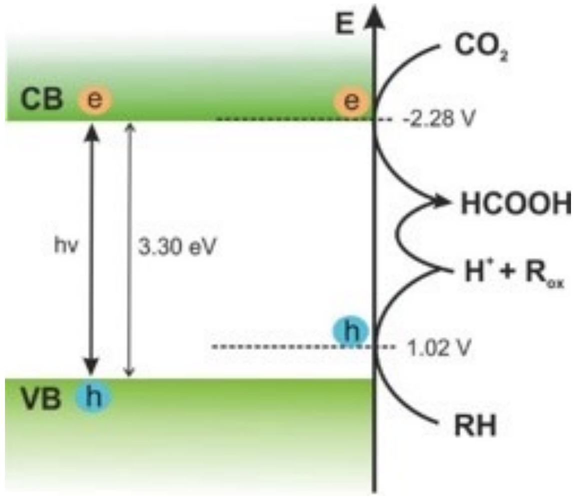
Alternative routes to large scale CO2R

- Water electrolysis via PV and use of PV-H_2 for CO_2 thermochemical conversion into energy products (CH_4, CH_3OH, others)

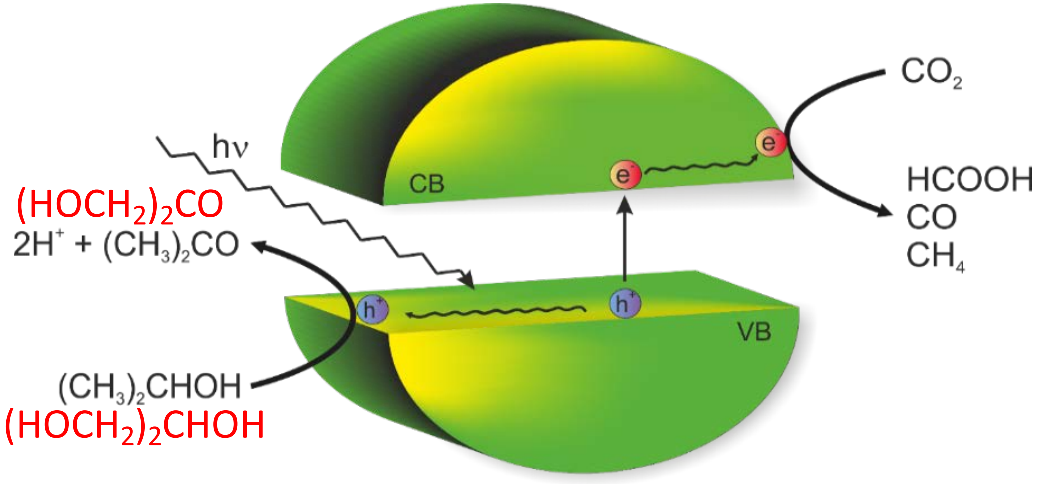
- CO_2 and water coprocessing in
  - Electrochemical reduction of CO_2, CO2ER (use of Cu electrodes for C2+ chemicals production: ethene, ethanol, others)
  - Photochemical co-processing of CO_2 and water to afford C1 and Cn species
  - Photo-electrochemical processing of CO_2 and water

D.M.S. Marcolongo, M. Aresta, A. Dibenedetto, Stepping Toward the Carbon-Circular Economy (CCE): Integration of Solar Chemistry and Biosystems for an Effective CO_2 Conversion into Added Value Chemicals and Fuels. *Advances in Inorganic Chemistry* Vol. 78 on Recent Highligths, Chapter 3, **2021**

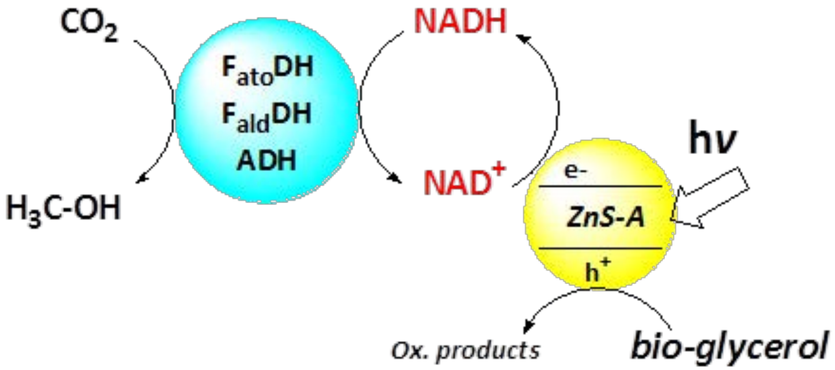
Use of solar energy and p-type SC in the direct CO_2 conversion



1. Photocarboxylation of organic substrates



2. Photoreduction of CO_2 in glycerol (i-propanol)-H2O with n-type semiconductors



3. Hybrid systems

ChemSuschem **2012**, 5, 2, 373–378, *Beilstein J. Org. Chem.* **2014**, 10, 2556–2565; *Applied Catalysis B: Environmental*, **2015**, 178, 170–176; *Chapter in: "From Molecules to Materials-Pathways to Artificial Photosynthesis*" Rozhkova, Elena A., Ariga, Katsuhiko (Eds.) (Springer), **2015**, *ChemSusChem* **2016**

Integration of Biotechnology and Catalysis

Let Nature fix CO_2 and Chemistry convert biomass

CO_2 → Aquatic, Land Biomass → Catalytic conversion

CO_2 → Bioglycerol → Products (oxidation, reduction)

CO_2 → Lignocellulose → Products (C6 and C5 polyols, aromatic fraction)

Catalysis as a tool for accelerating bioprocesses

BES for *in situ* providing hydrogen for CO_2 conversion to C1, C2, Cn molecules

M. Aresta, A Dibenedetto, F. Dumeignil "*Biorefinery: from biomass to chemicals and fuels*" **2021**, De Gruyter, in press

Microalgal biomass is compatible with the integrated **Biorefinery Vision** of producing a variety of valuable products and fuels.

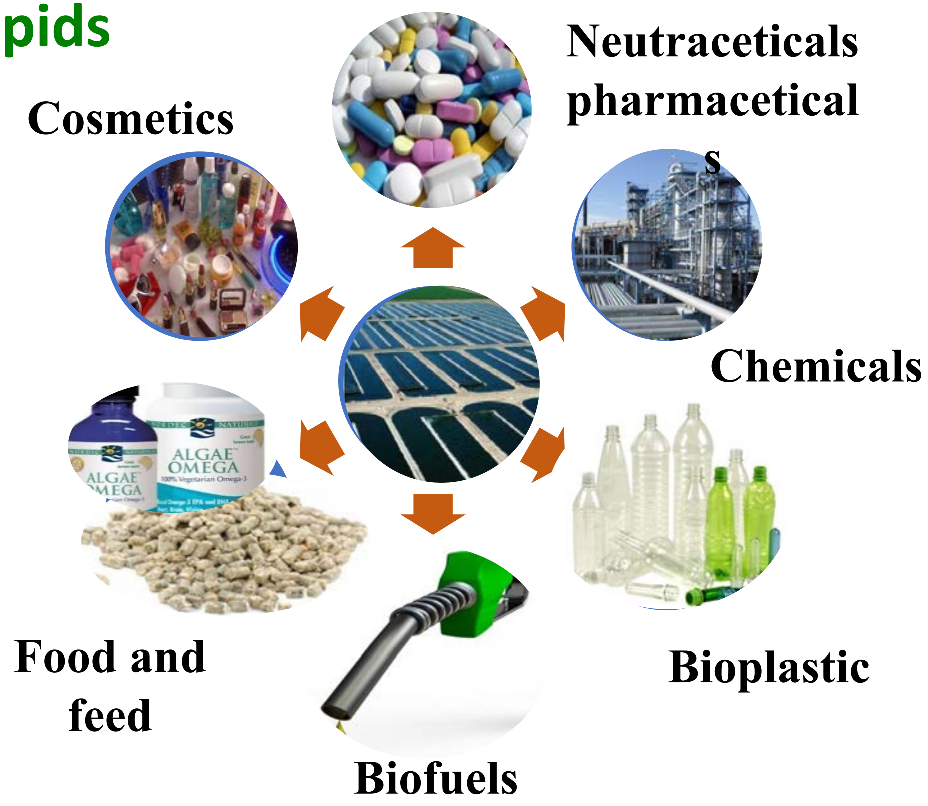
Using algae only for making fuels (liquid and gas) is not economic

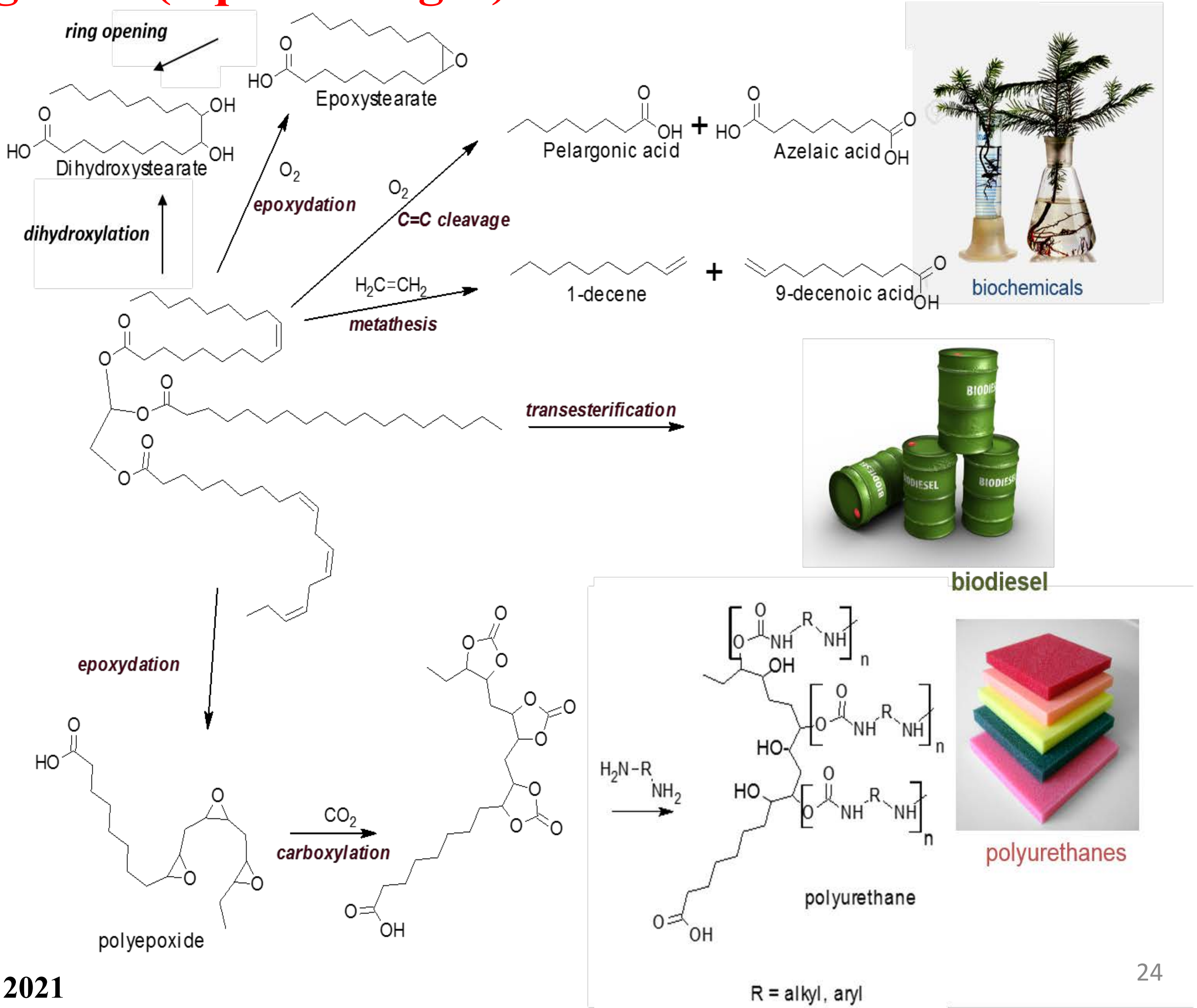
Fractionation:

Cellulose (no lignin)

Proteins

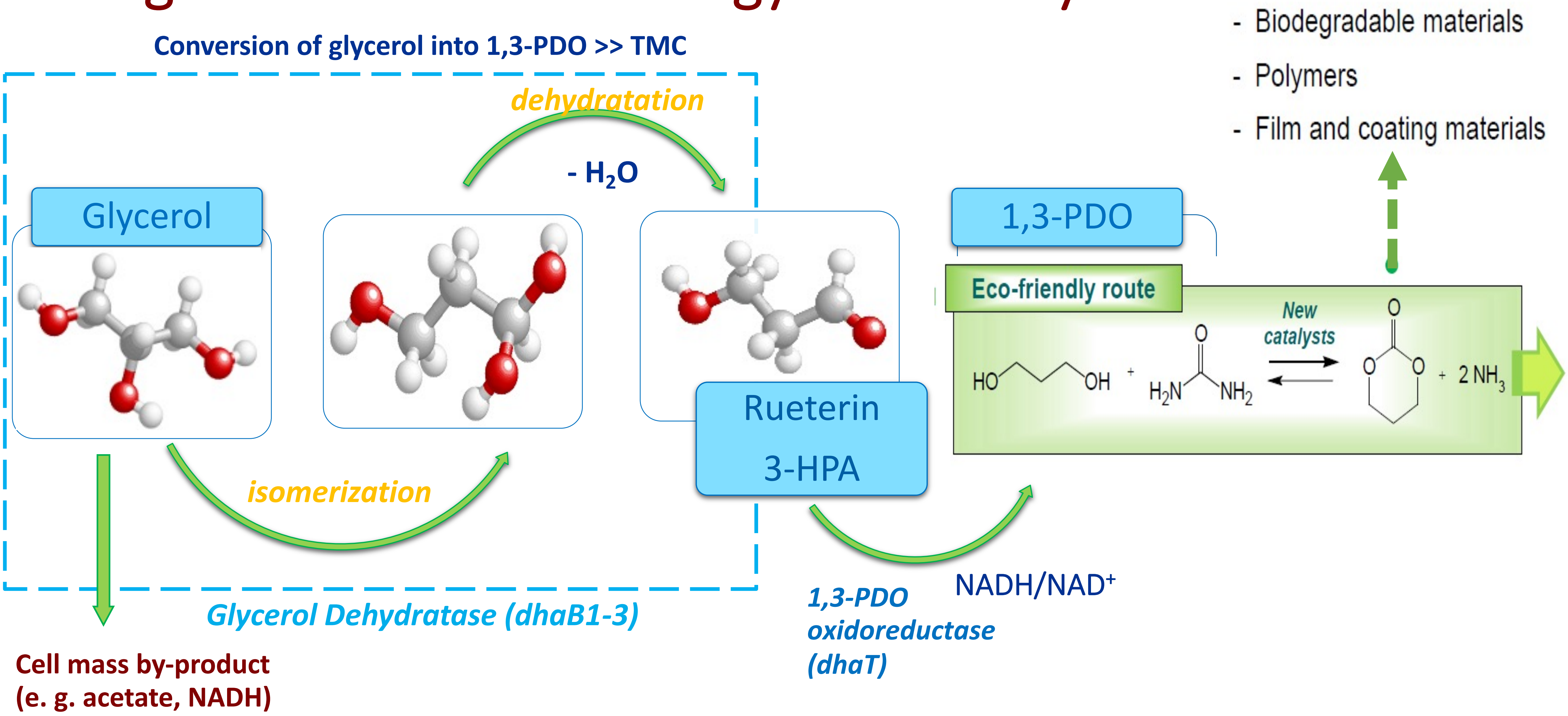
Lipids





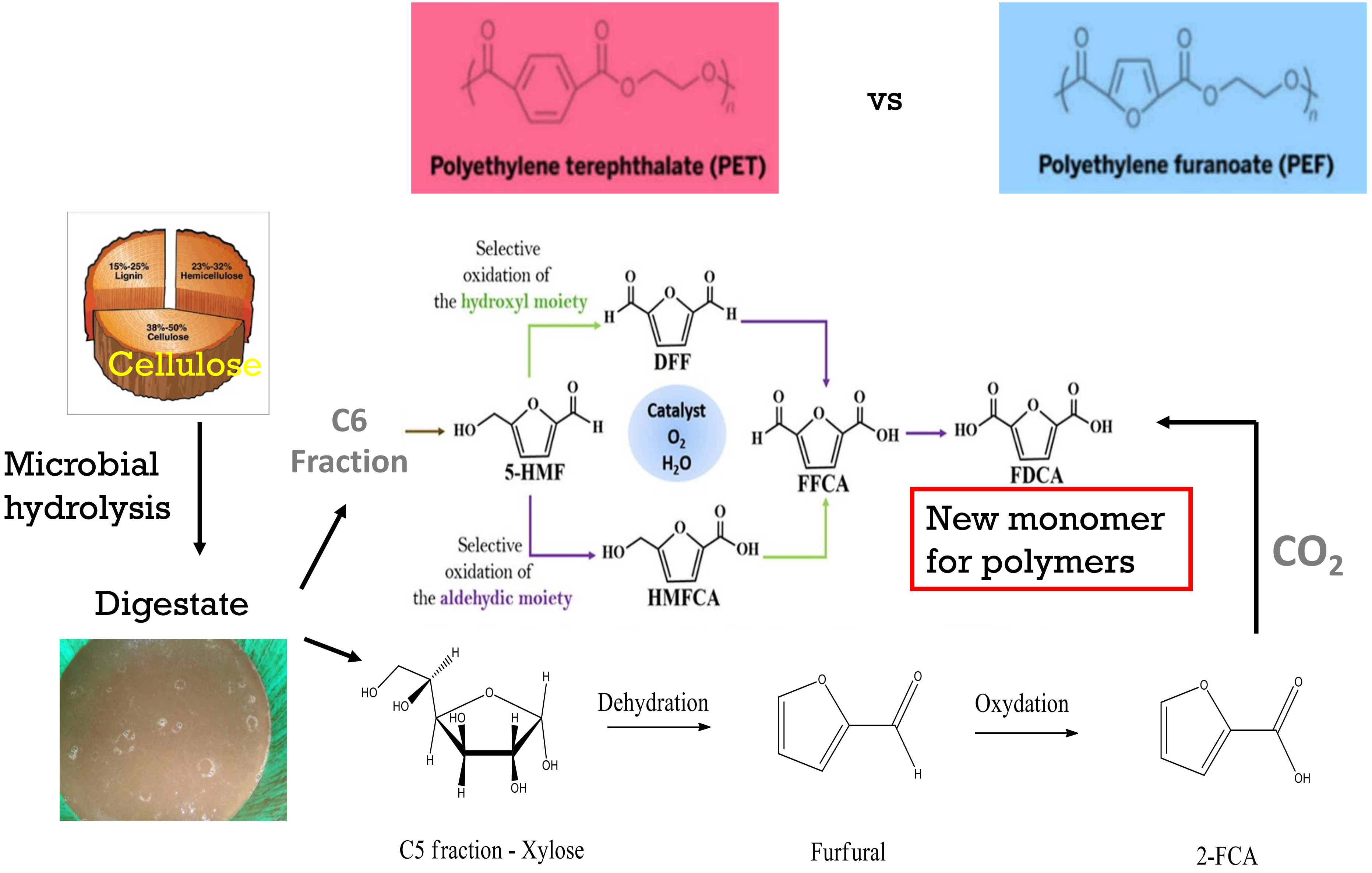
Dibenedetto et al. *J Cat* **2016,** *ACS Sustainable Chemistry & Engineering* **2021**

Integration of Biotechnology and Catalysis



A. Dibenedetto, M. Aresta, L. di Bitonto, J. L. Dubois, *Patent EP 13192912.7*, **2013**

Integration of Biomass and CO_2 utilization, Biotechnology and Catalysis

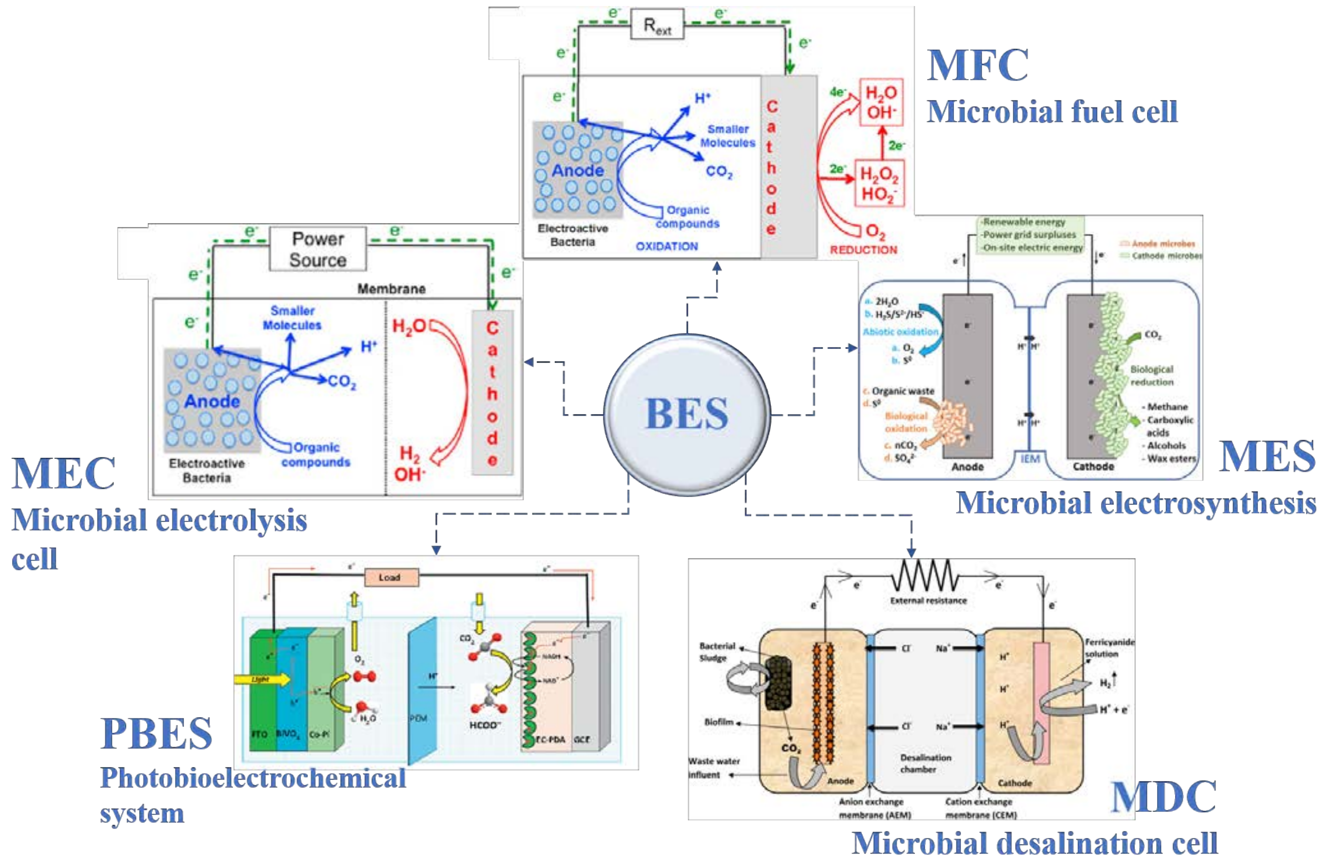


Dibenedetto et al. *ChemSusChem* **2016**; Patent MI102016000014339, **2016**; *Inorg Chimica Acta* **2018**; *ChemSusChem* **2018**; *Green Chemistry* **2018**; *ACS Omega* **2018**, *JCOU* **2019**

Bioelectrochemical systems-BES

BES have recently been proposed as a new and sustainable technology for energy generation and useful products from wastes: in a BES, bacteria interact with solid-state electrodes by exchanging electrons with them, either directly or via redox mediators.

$CO_2 \rightarrow$ Methane,
Carboxylic acids,
Alcohols,
Wax esters,
Formic acid, …..



D.M.S. Marcolongo, M. Aresta, A. Dibenedetto *Advances in Inorganic Chemistry* Vol. 78 on Recent Highligths, Chapter 3, **2021**

Conclusion

- **CO_2 is a valuable source of carbon**: it is already used in the chemical industry at a rate of **200 Mt/y**.
- Using the existing knowledge the expectation is to convert over **370 Mt/y** by 2030 avoiding >1000 Mt/y
- Nature makes from CO_2 thousands energy-rich compounds using solar energy
- The combination of the use of solar energy with CO_2 catalytic conversion may bring to the reduction to fuels, enlarging the utilization to a several Gt/y level, with concomitant reduction of extraction of fossil-C.
- Hybrid catalysis and biotech may open a new scenario in CO_2 conversion into energy products.


Thank You!