DE LA RECHERCHE À L'INDUSTRIE

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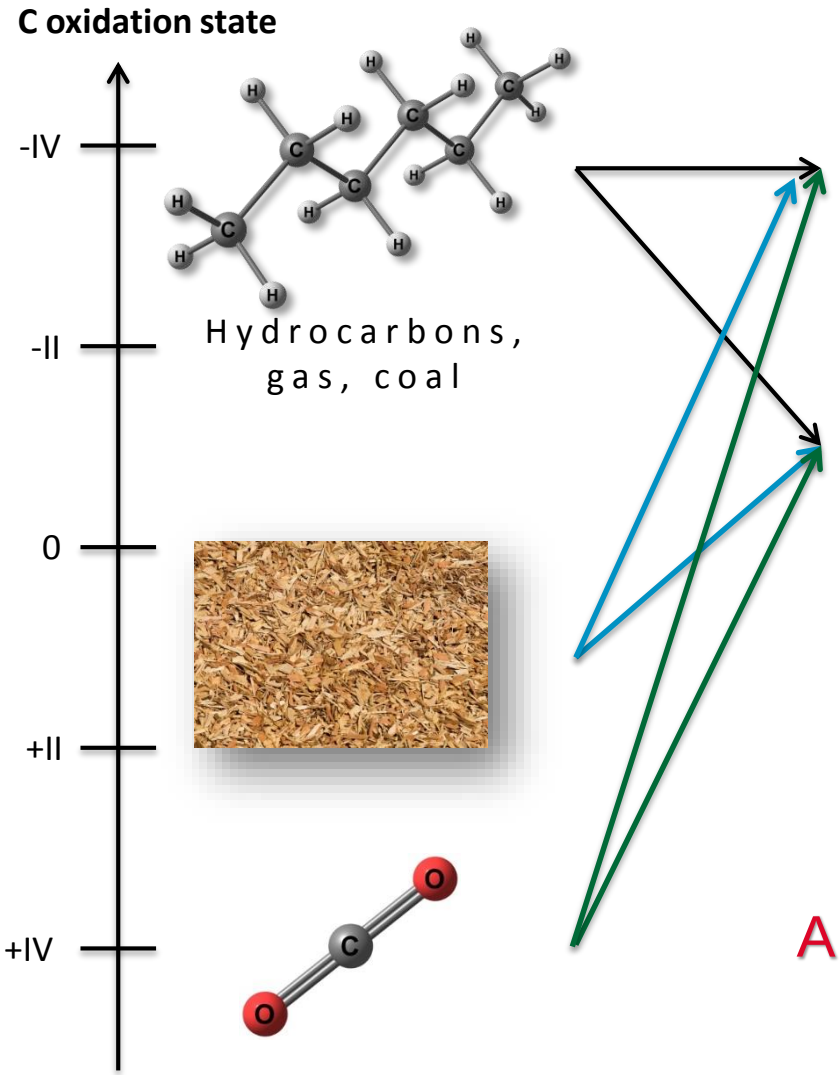
CO_2 AND BIOMASS CONVERSION: SCIENTIFIC CHALLENGES AND OPPORTUNITIES

CEA / CNRS | Thibault Cantat

WORKSHOP SCIENTIFIQUE
EDF / UNIVERSITÉ PARIS SACLAY
OCTOBER 5 – 2016

CARBON SOURCES HAVE DIFFERENT ENERGY CONTENTS

Carbon feedstocks



Applications

Fossil carbon fuels

80% of the world energy portfolio

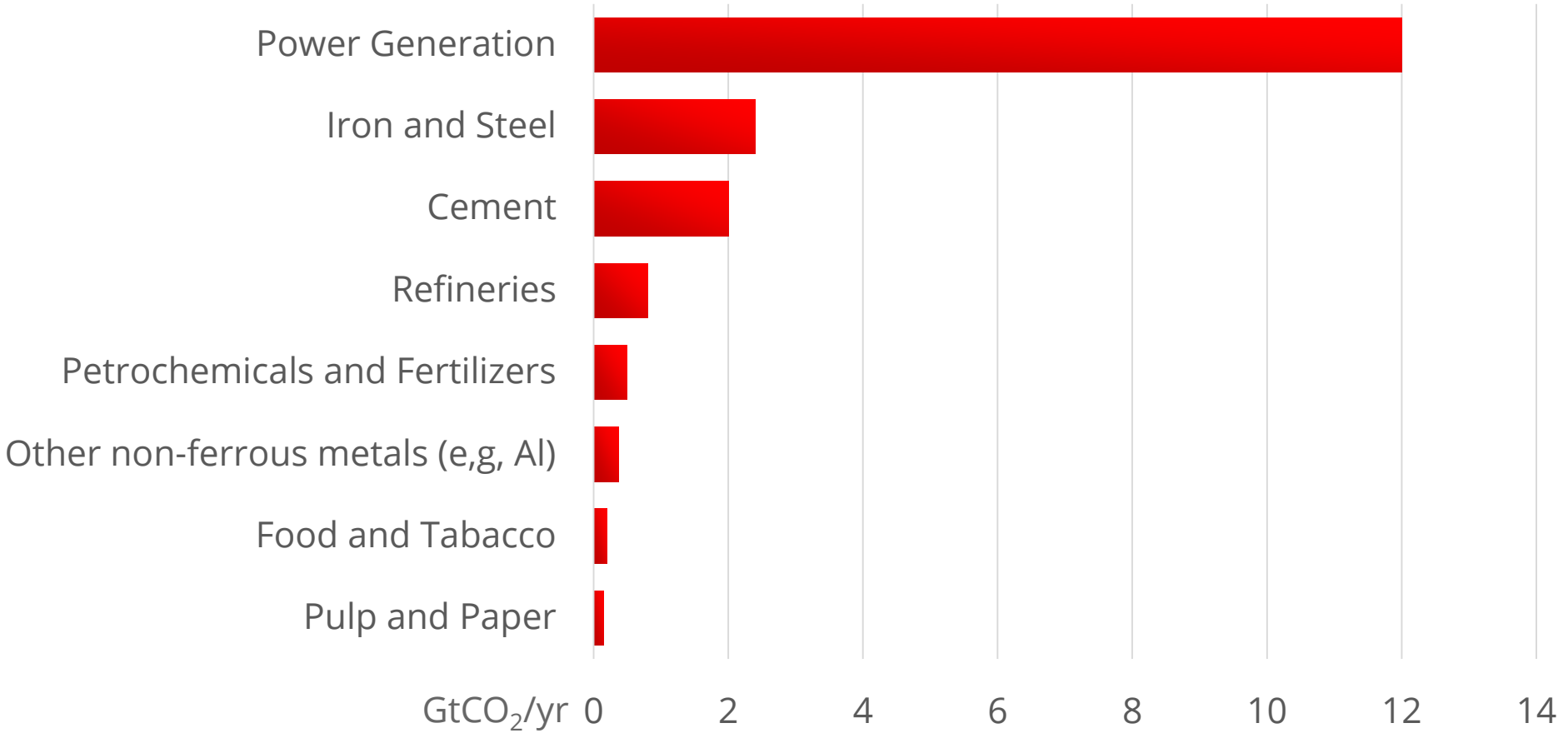
Chemicals

95% of organic chemicals derive from fossil feedstocks

A paradigm shift: oxidation vs reduction

CO_2 EMISSIONS – FIGURES WORLDIDE

World CO_2 emissions by industry



Source: IEA

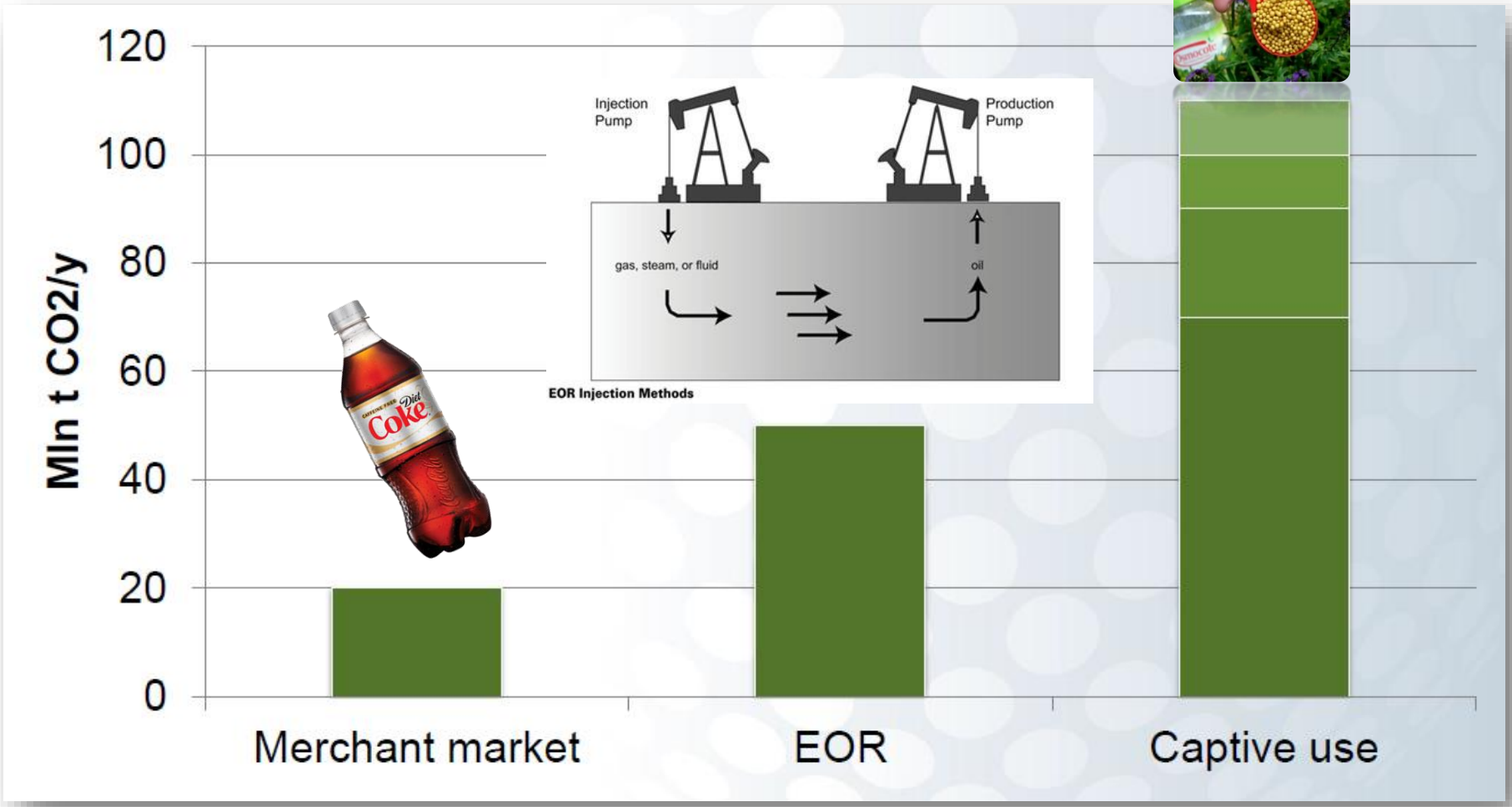
CO_2 SOURCING TODAY

Guidelines

- High CO_2 content in raw gas (>90% of CO_2) preferable due to energy penalties by concentration
- Small amount of contaminants
- Long term commitment with raw CO_2 supplier
- Reliable raw CO_2 source
- Favorable logistics

CO_2 UTILIZATION TODAY

Guidelines



Food, beverages, etc.

Enhanced Oil Recovery

CO_2 to chemicals

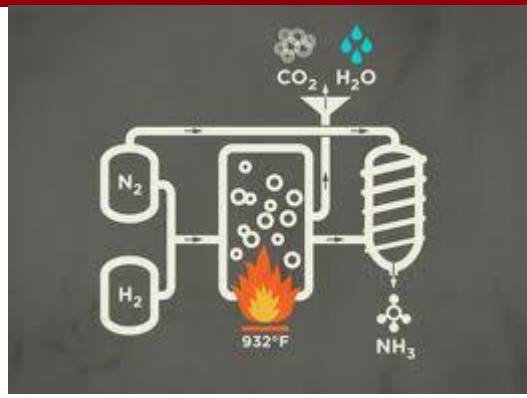
CO_2 SOURCING TODAY

Ammonia

- As byproduct from hydrogen production for the Haber-Bosch process
  (e. g. steam reforming of hydrocarbons)

  $CH_4 + 2\ H_2O = CO_2 + 4\ H_2$

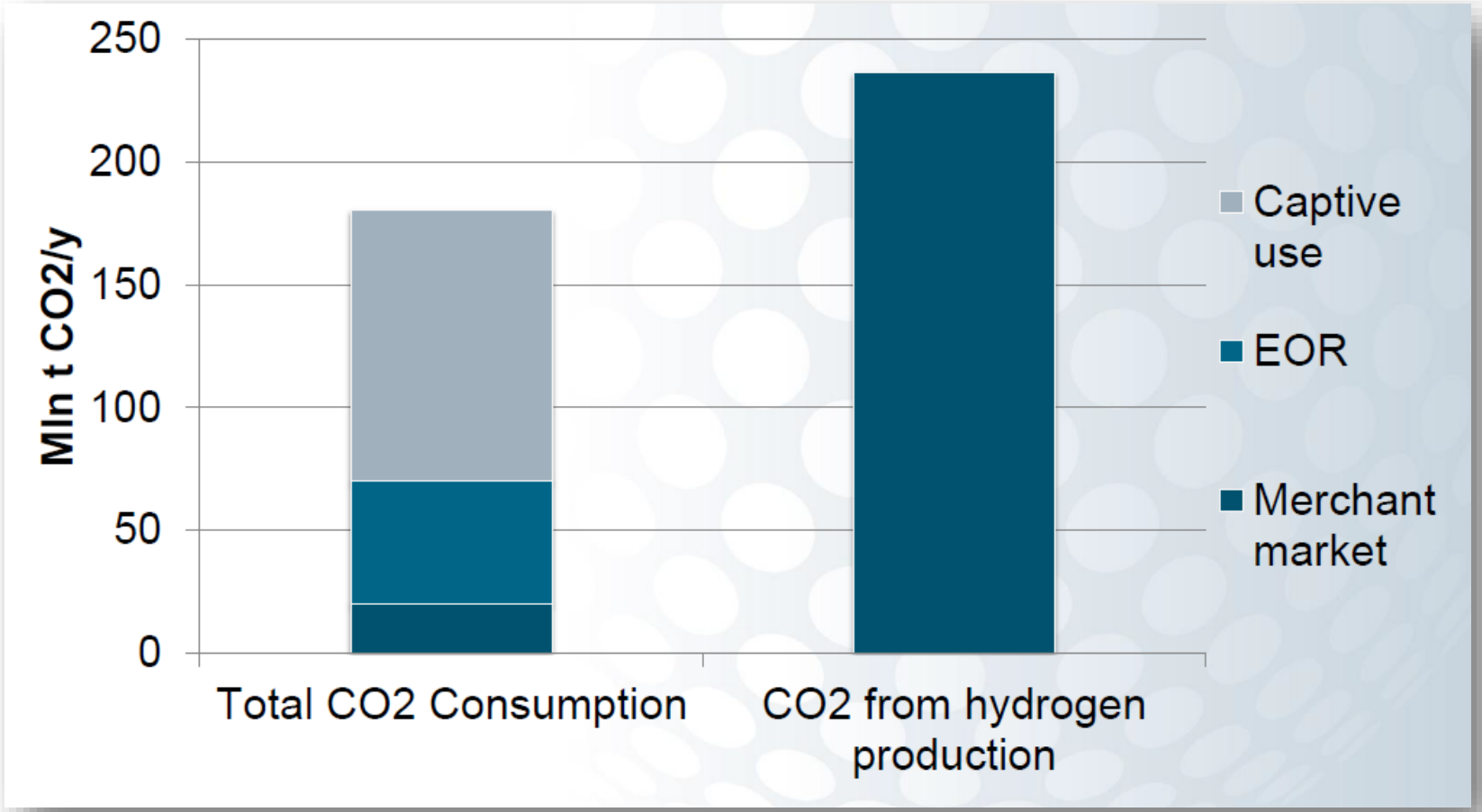
- High CO_2 content in raw gas (>98% of CO_2)
- High reliability
- Low on contaminants
- Often placed in industrial zones, close to large consumers
- Approximately half of European merchant CO_2 supply
- Approximately 70% of world captive use (urea)



~2% of the world's annual energy supply

CO_2 SOURCING TODAY

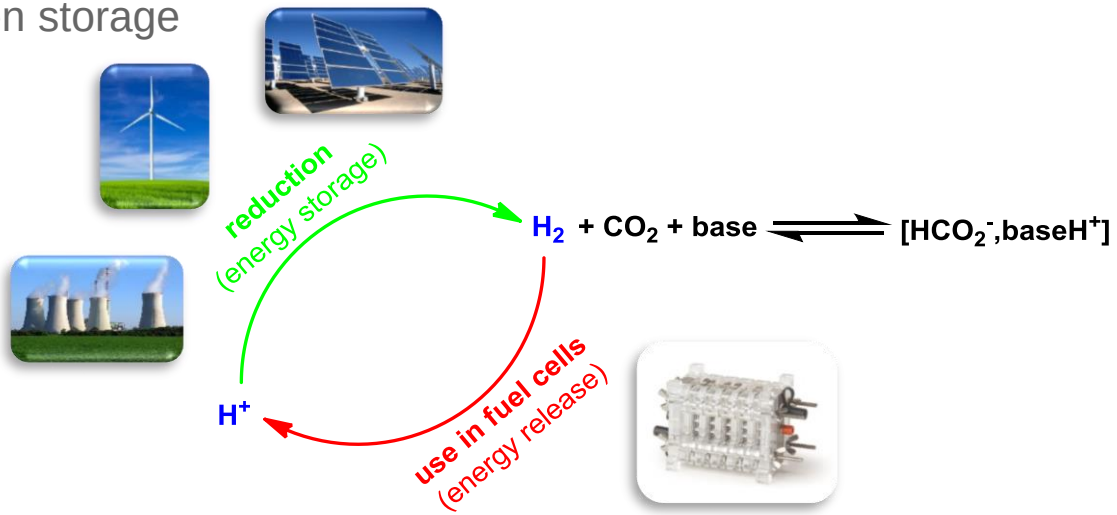
Ammonia



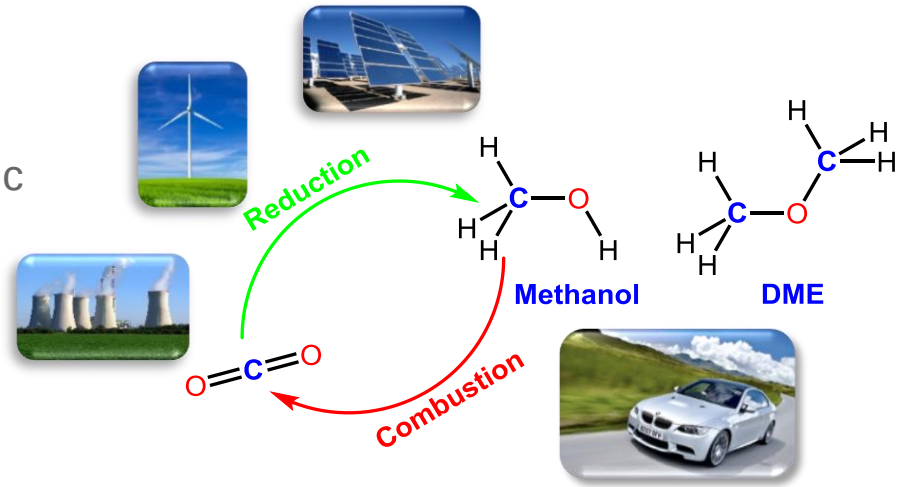
CO_2 AS AN ENERGY VECTOR

CO_2 reduction: recycling to fuels

- CO_2 hydrogenation for hydrogen storage
  - CO_2 to formic acid
  - CO_2 to methanol

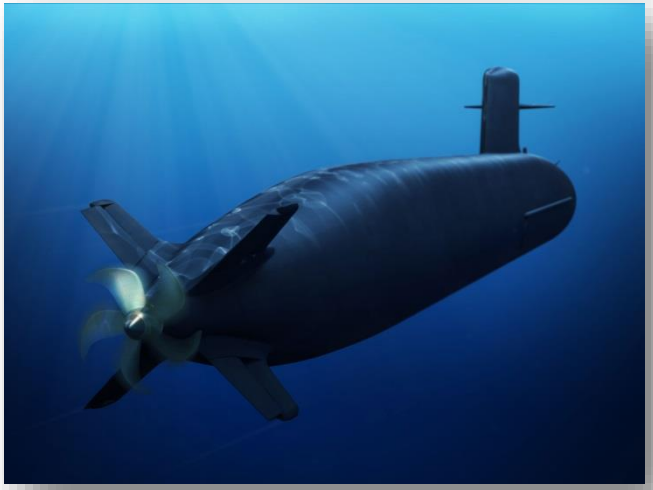


- CO_2 electro- and photoelectro-catalytic reduction to CO, formic acid, methanol, etc.



CO_2 TO FUELS: ALREADY INDUSTRIALIZED?

Limited short terms opportunities



$$H_2O \longrightarrow H_2 + {}^1/_2\, O_2$$

$$H_2 + CO_2 \longrightarrow CH_3OH + H_2O$$

methanol

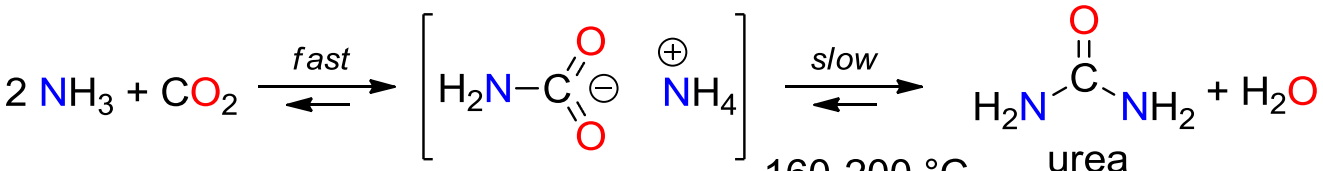
European Directives:

- Renewable Energy Directive
- Fuel Quality Directive

INDUSTRIAL PROCESSES UTILIZING CO_2

Industrial routes from CO_2

- Bosch-Meiser process for urea production



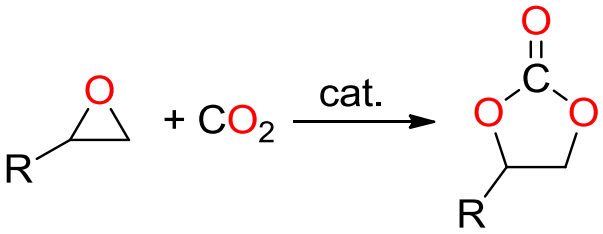
120 Mt/y

- Inorganic carbonates

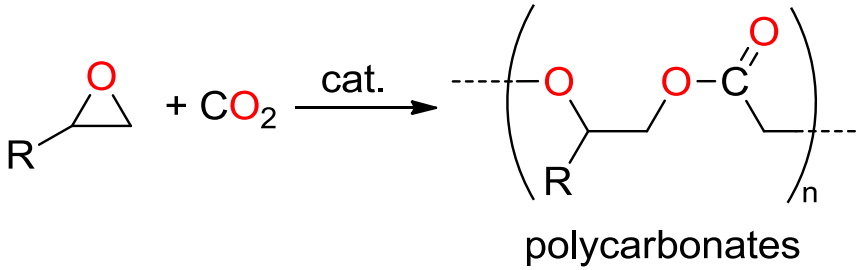
for CCS applications

44 Mt/y

- Synthesis of cyclic and polymeric carbonates



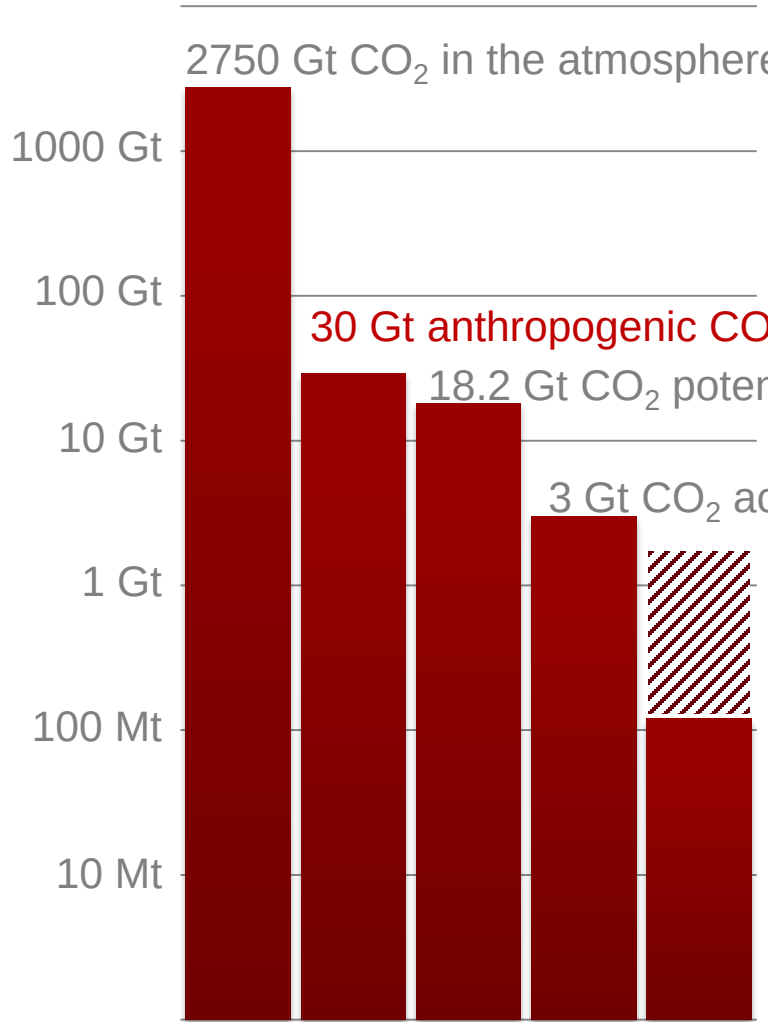
150 kt/y



65 kt/y

CO_2 TO VALUE ADDED CHEMICALS

Market opportunities with no significant impact on CO_2 emissions



Conversion of CO_2 to chemicals is NOT a solution to the greenhouse effect

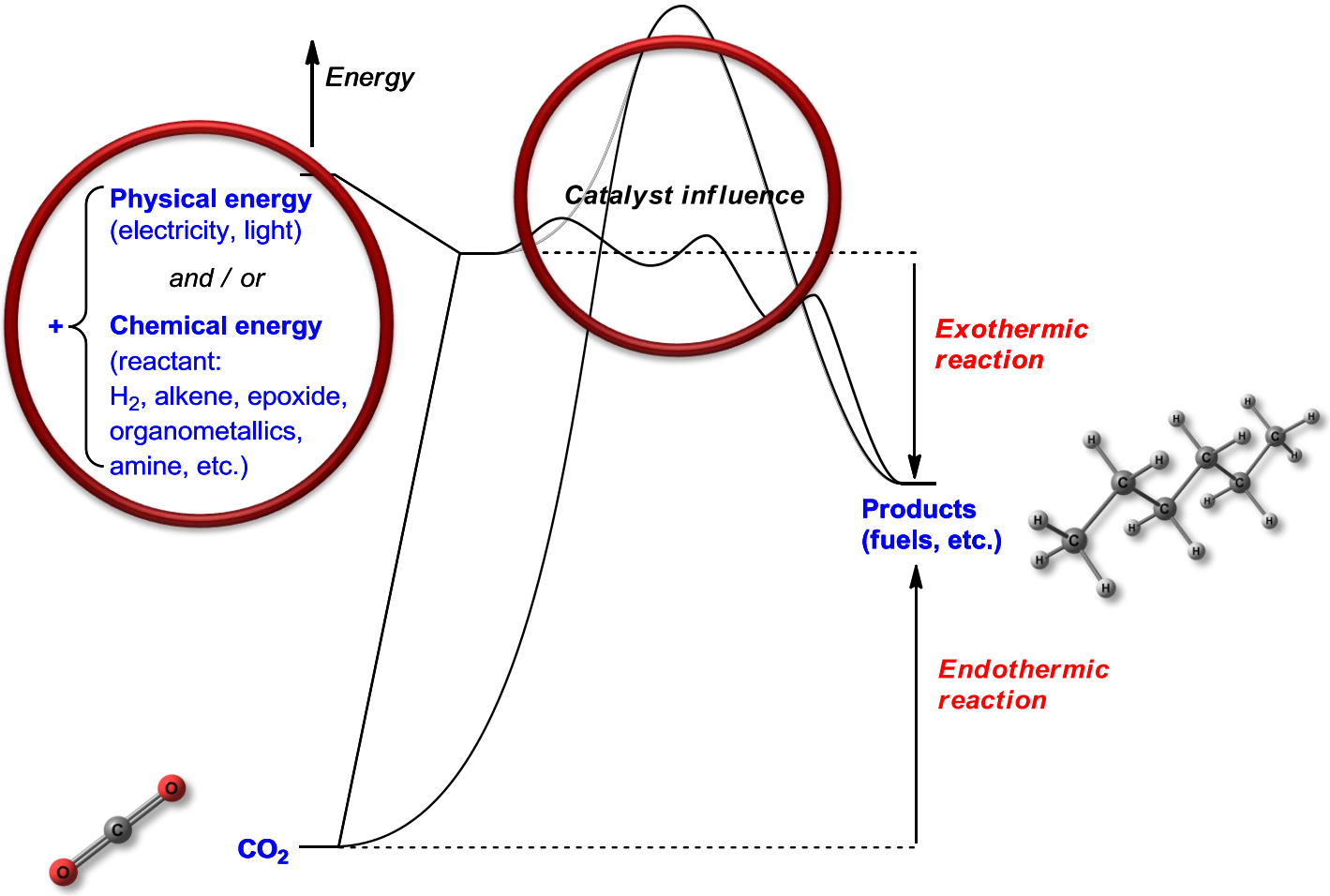
BUT:

- CO_2 is a cheap, secured, renewable and well-distributed carbon feedstock
- CO_2 can replace toxic reagents (phosgene, isocyanates, etc.)
- Short terms opportunities in bulk chemicals to fine chemicals

Multiple markets, multiple targets: need for multiple new processes

Cantat et al., *Green Chem.* **2015**, *17*, 157.

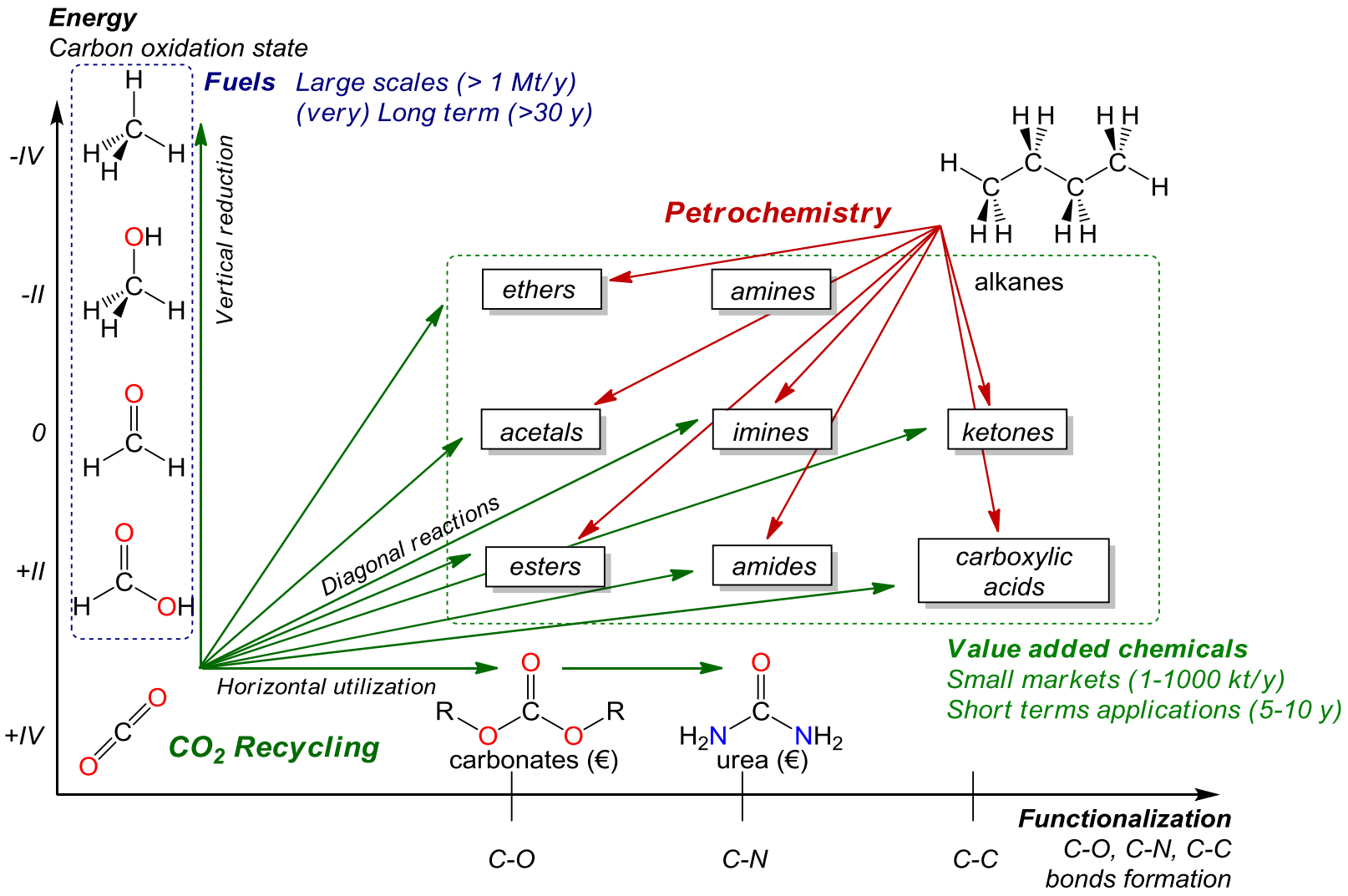
CHEMICAL TRANSFORMATION OF CO_2



Two energetic challenges: thermodynamic **and** kinetic

A DIAGONAL APPROACH

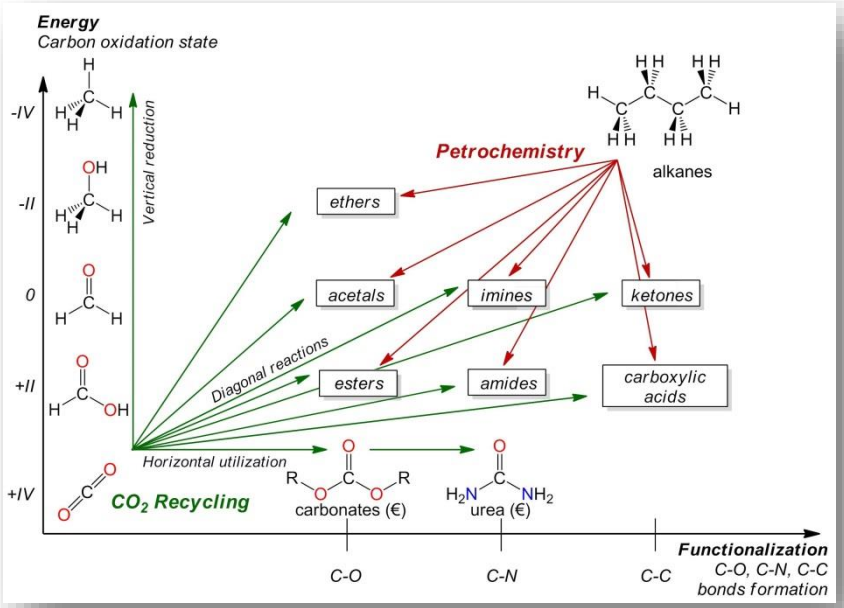
VARIOUS OPPORTUNITIES TO CO_2 RECYCLING…

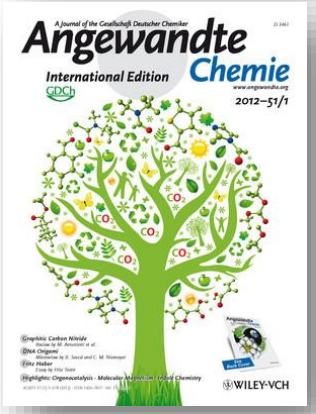


Objective: develop efficient and viable catalytic processes

PROOF-OF-CONCEPT: NEW CATALYTIC PROCESS

Proof-of-concept for the diagonal approach

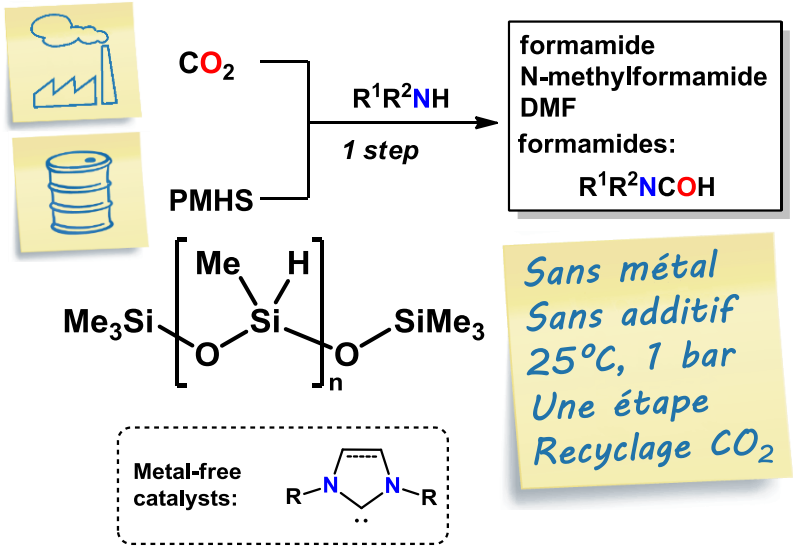




- Cover picture in **Angewandte Chemie**
- **Very Important Paper** (top 5%)
- Highlighted in **Nature**

Co-recycling CO_2/PMHS (CEA/DSM technology)

Metal-free catalysts, room temperature, single step



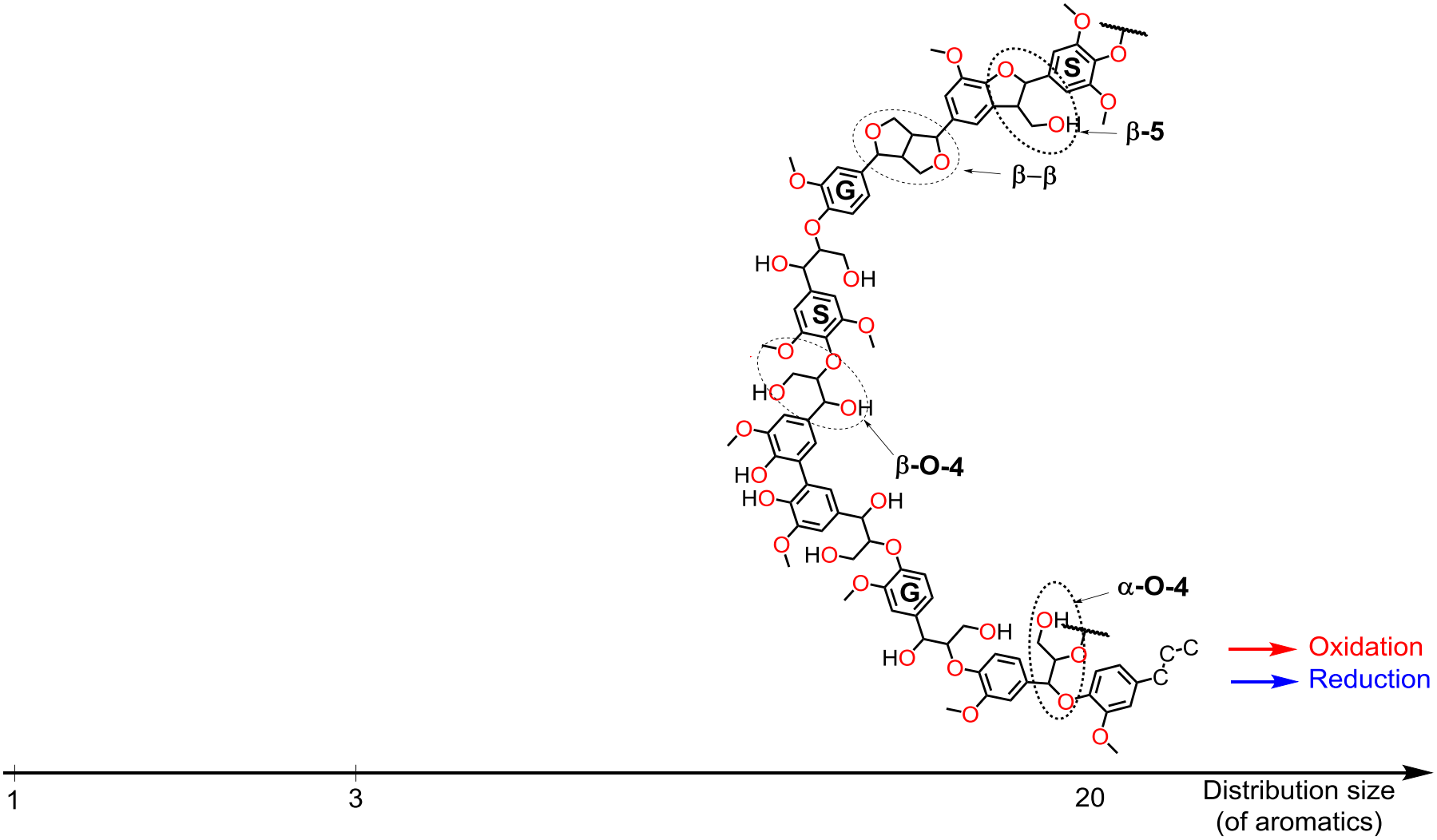
Sans métal
Sans additif
25°C, 1 bar
Une étape
Recyclage CO_2

World production: 500 kt/y from oil
Utilization as solvents and reactants

- CO_2 as an alternative to petrochemistry
  Utilization of an energy vector (H, Si) coupled with a functionalizing reactant

Cantat et al., *Angewandte Chemie* **2012**, *JACS* **2012**, WO2012137152

CONVERGENT REDUCTIVE DEPOLYMERIZATION



Cantat et al., *Energy Environ. Science,* **2015**, 8, 2734
For lignin oxidation see: Weckhuysen et al. *Chem. Rev.*, **2010**, *110*, 3552
Stahl et al. *Nature* **2014**, 515, *J. Am. Chem. Soc.* **2013**, 135, 6415

LIGNIN REDUCTION TO CHEMICALS

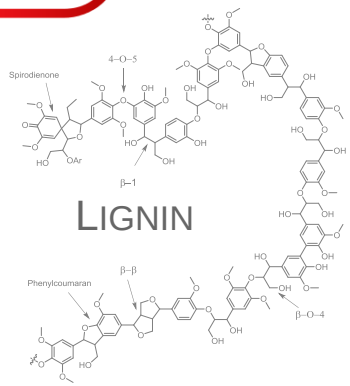
Lignin reductive depolymerization

- CEA Technology: CALRED Process

Production of analytically pure aromatic compounds (catechols) from wood

CALRED

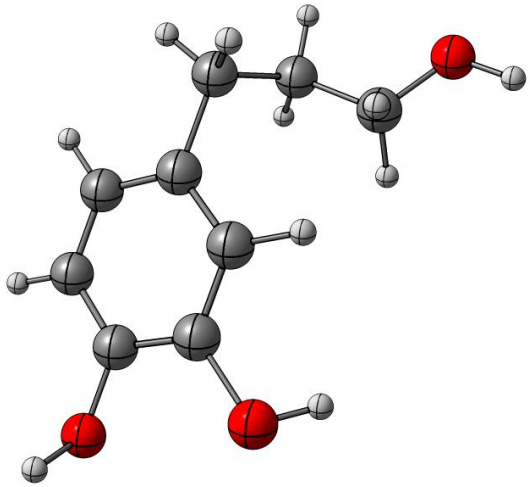
15 wt%



LIGNIN

20 wt%

Metal free
Additive free
25°C, 16 h
Recycling of PMHS, TMDS

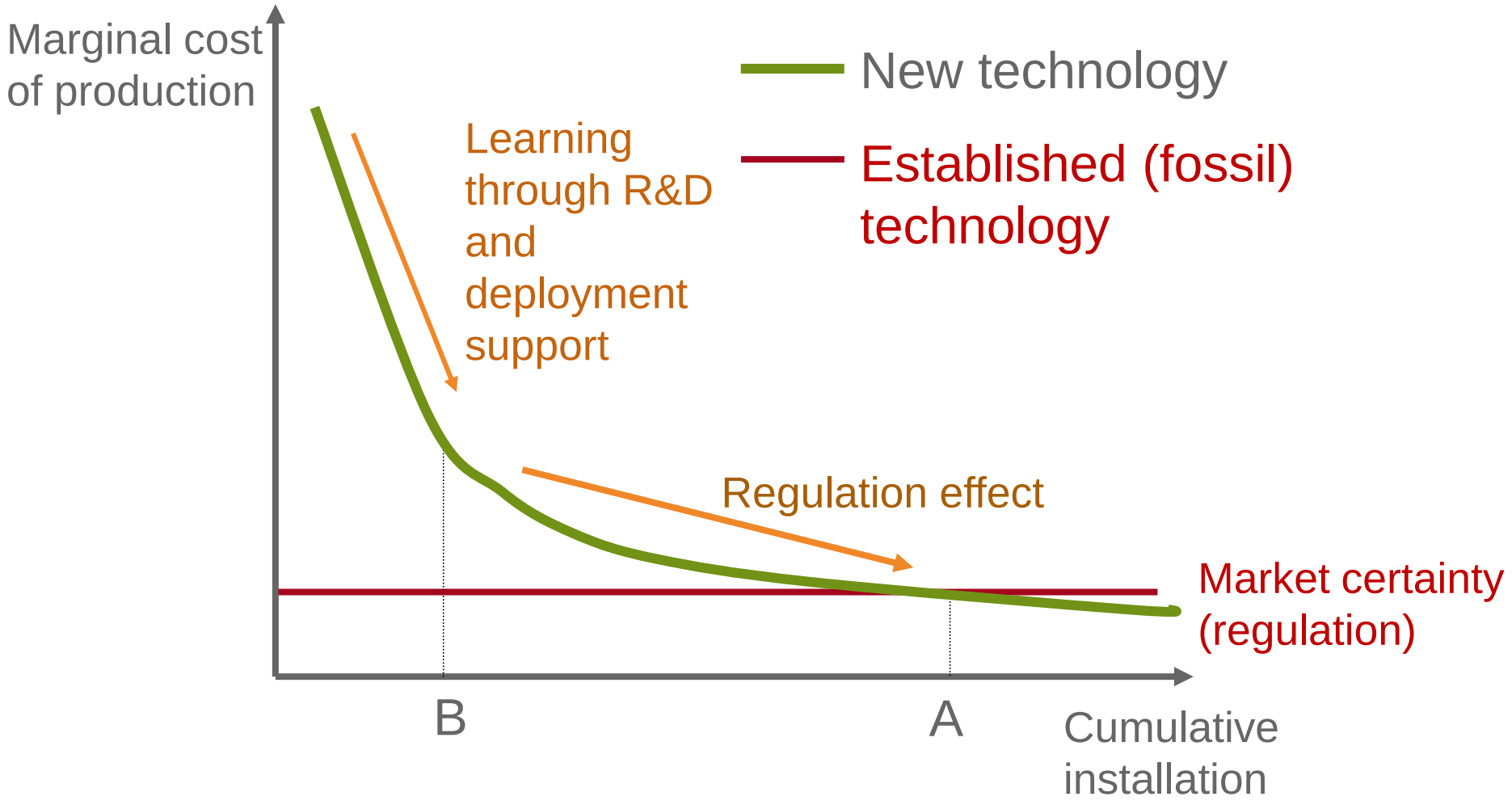


PURE AROMATIC COMPOUNDS

Cantat et al., *Chem. Commun.* **2014**, *50*, 862; *Energy Environ. Science,* **2015**, 8, 2734; patents WO2016005836; WO2016005837

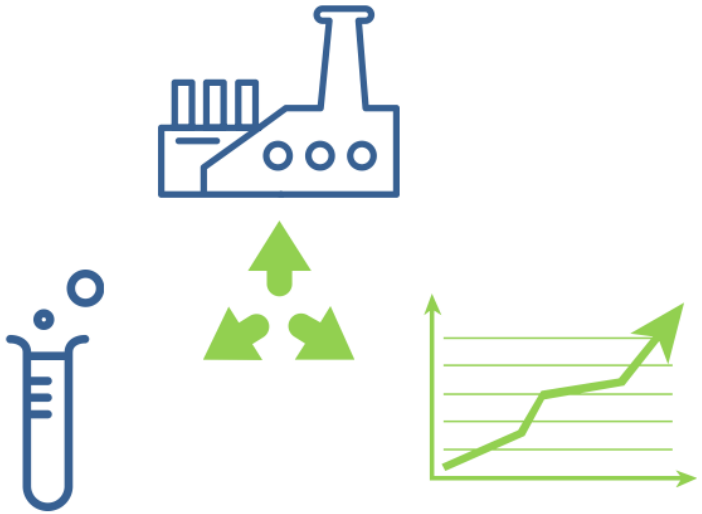
CO_2 DYNAMIC

Interaction between policy instruments



THE VALUE OF CO_2

- Market vision
- Innovation in CO_2 reduction



- Environmental constraints
- Political strategy and regulations
- Social sciences and humanities

- Basic research
- Applied research
- Co-developments

RECYCLING STRATEGIES

REWEAR
CLOTHING THAT CAN BE WORN AGAIN IS MARKETED WORLDWIDE AS SECOND-HAND GOODS.

REUSE
TEXTILES THAT ARE NO LONGER SUITABLE TO WEAR ARE CONVERTED INTO OTHER PRODUCTS, SUCH AS CLEANING CLOTHS.

ENERGY
WHEN REWEAR, REUSE AND RECYCLE ARE NOT OPTIONS, TEXTILES ARE USED TO PRODUCE ENERGY.

RECYCLE
TEXTILES THAT CAN'T BE REUSED GET A NEW CHANCE AS TEXTILE FIBRES, OR ARE USED TO MANUFACTURE PRODUCTS SUCH AS DAMPING AND INSULATING MATERIALS FOR THE AUTO INDUSTRY.

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