


Carbon Dioxide to Chemicals Beyond Utopia

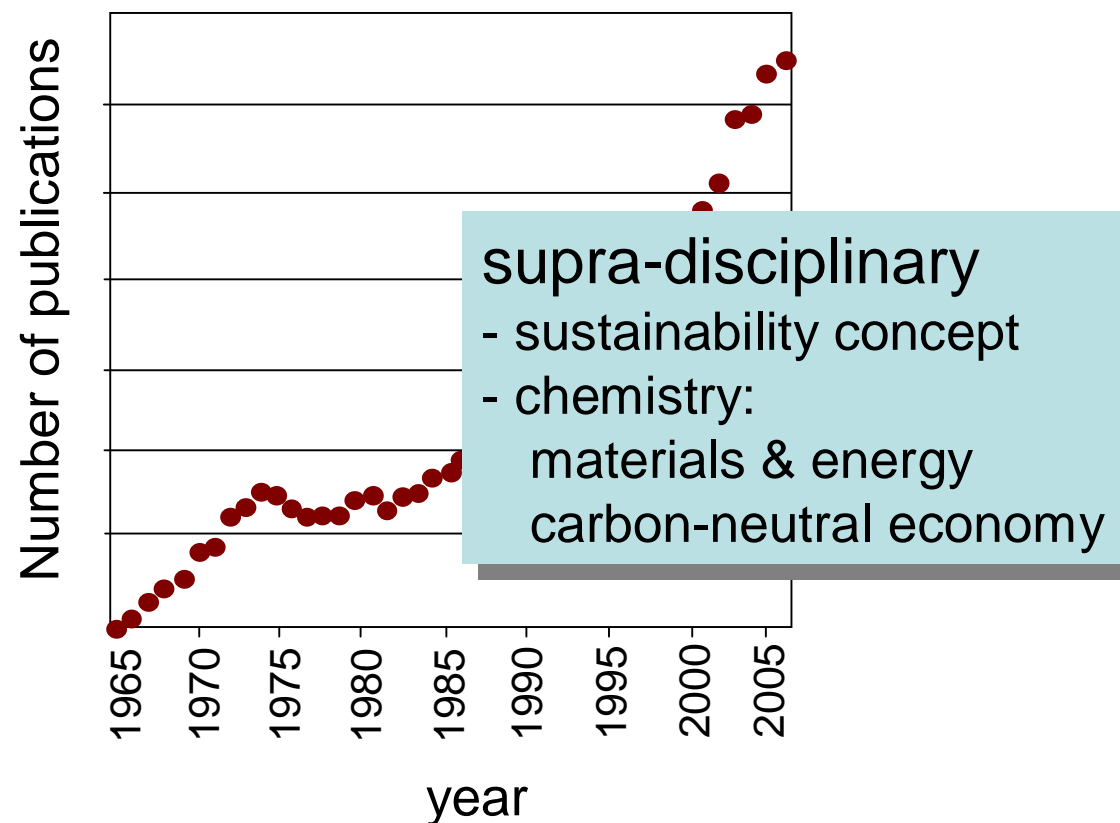


Danielle BALLIVET-TKATCHENKO

*Institut de Chimie Moléculaire
CNRS-Université de Bourgogne*

CO₂-related publications

SciFinder[®] database





Outline

- Facts & figures
- CO₂ in synthesis
challenges
achievements
needs
- Outlook

CO₂ facts and figures

- Greenhouse gas contribution = 50%
- < 50% remains in the atmosphere (half-life 5 years)
- Two major anthropogenic fluxes
 - fossil fuel combustion, industrial process
 - land-use change
 - 1990s 1% increase per year
 - **2000-2005 3%**
- Developing and less-developing economies
 - 80% of the world population
 - **73% of global emission growth in 2004**

Mitigation measures

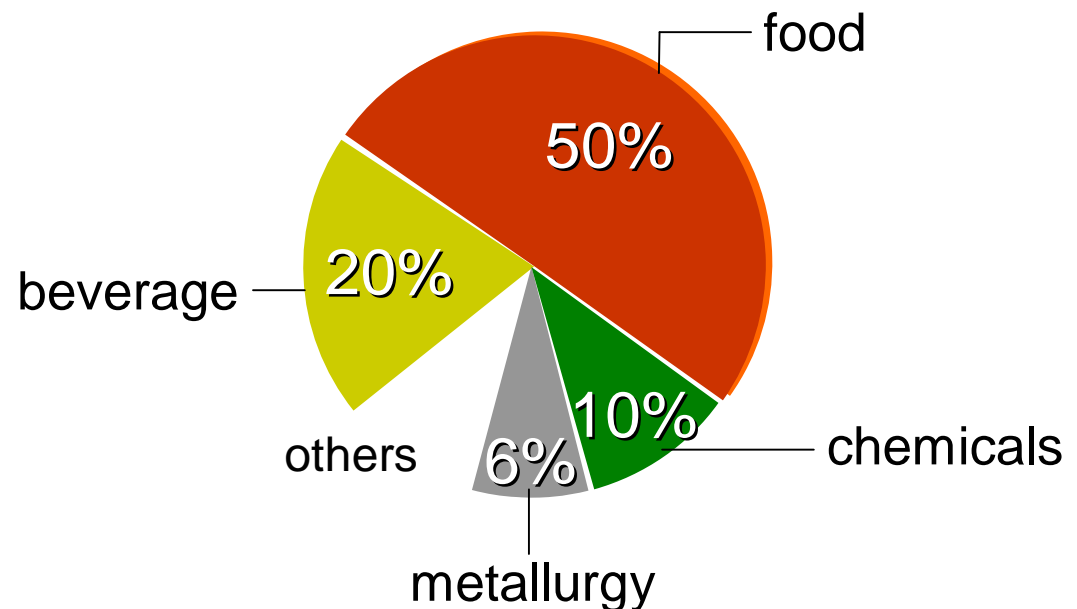


- Decarbonization of energy supply
- CO₂-neutral energy supply
- CO₂ utilization
- ...

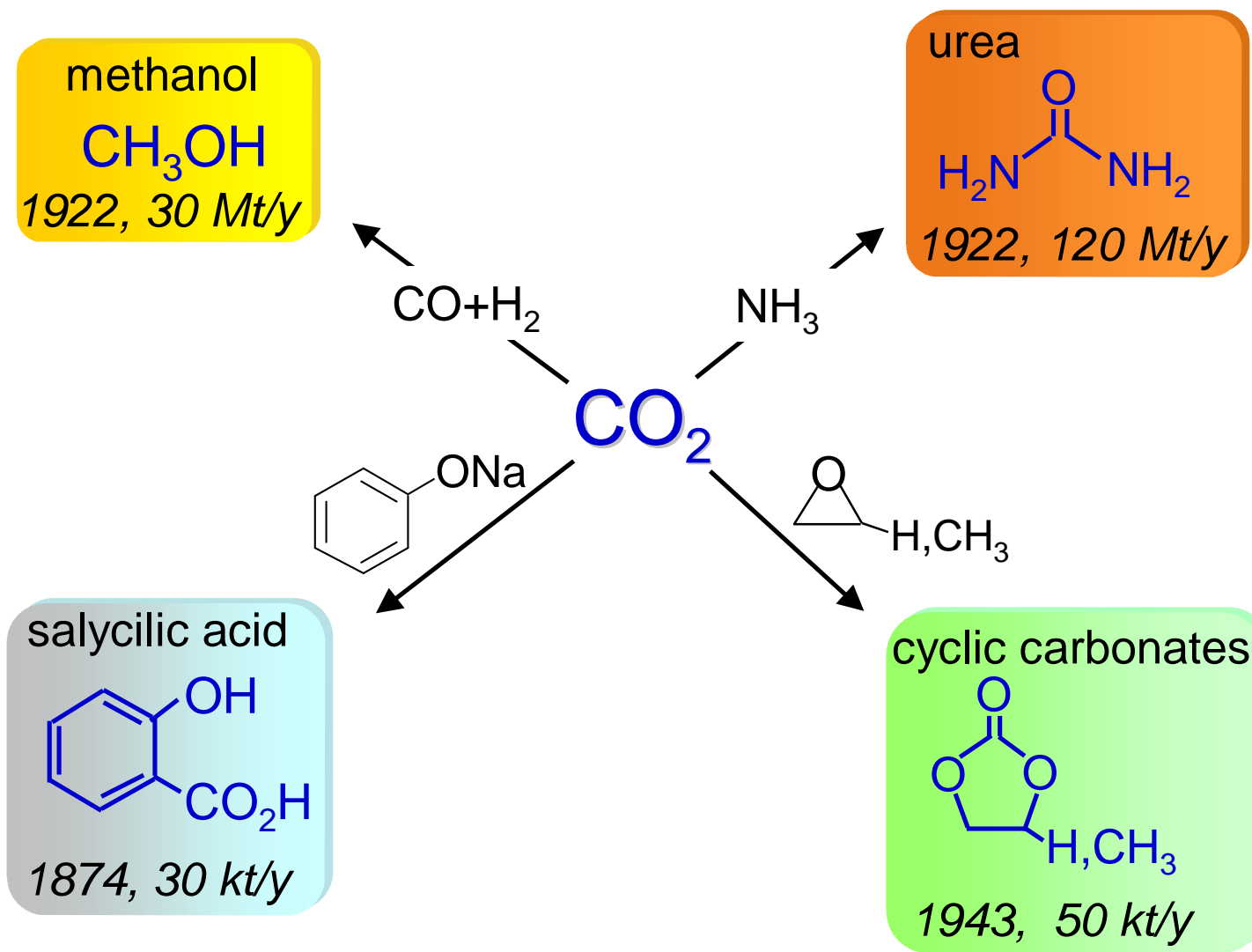
Current applications

Gas, Liquid & Solid

- **90%**
 - CO₂-Enhanced Oil Recovery
 - Urea synthesis
- **10%**
 - Refrigeration
 - Extraction
 - Protection
 - Chemistry



On-stream processes to chemicals



CO₂ to chemicals

- Large-scale use of CO₂ is challenging
 - market size
 - energy input
- Industrial use of CO₂
≈140 Mt/y, 2 % of anthropogenic CO₂ emission
- Chemicals
≈700 Mt/y
- Photosynthesis billions tons/y of cellulose

CO₂ for chemistry

- Chemically "inert"

ΔG_f^0 kJ mol⁻¹ for key carbon compounds

C ₆ H ₆	+130
C ₂ H ₄	+68
CH ₄	-51
HCHO	-102
CO	-137
CH ₃ OH	-166
HCOOH	-361
NH ₂ COOH	-364
CO ₂ (g)	-374
CO ₂ (aq)	-386

CO₂ for chemistry

- Chemically "inert"

 - Challenges

 - reactions
 - active catalysts
 - catalyst development

- Cheap

- Ideal chemical - *green reagent*

 - low toxicity, non-flammable, abundant
 - an alternative source of carbon
 - a renewable resource by recycling

3E criterion

Efficiency of synthetic methodology

Economical viability for industrial production

Environmentally benign

Reagents
Products
Solvents
Reaction conditions

CO₂ a green solvent



2001, Thomas Swan & Co (UK)

Multipurpose production
2000 t/y

- hydrogenation
- hydroformylation
- etherification
- esterification
- alkylation

Some benefits

- *heterogeneous catalysts*
- *continuous flow reactor*
- *solvent-free products*
- *productivity/selectivity*



CO₂ a safer feedstock

Phosgene: COCl₂

methanol
ethanol
n-butanol

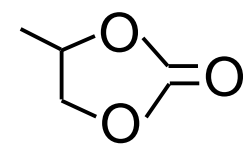
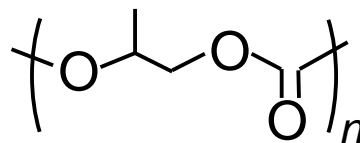
phenol

bisphenol-A

ethylene glycol
propylene glycol



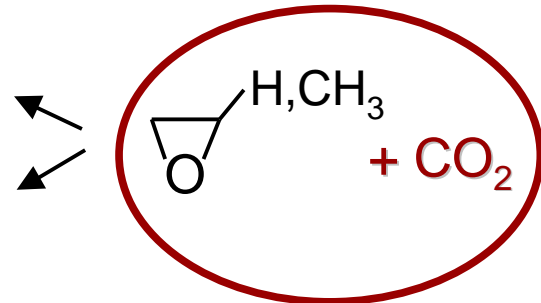
PO...OP
polymers
solvents
cosmetics
lubricants
pharmaceuticals
fabrics
fuel additives



Alternatives

methanol + CO + O₂

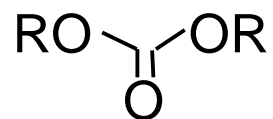
transesterification



CO₂ a safer feedstock

Phosgene

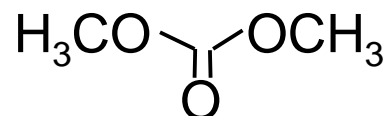
methanol
ethanol
n-butanol



Alternatives

← methanol + CO + O₂

scale-up production?

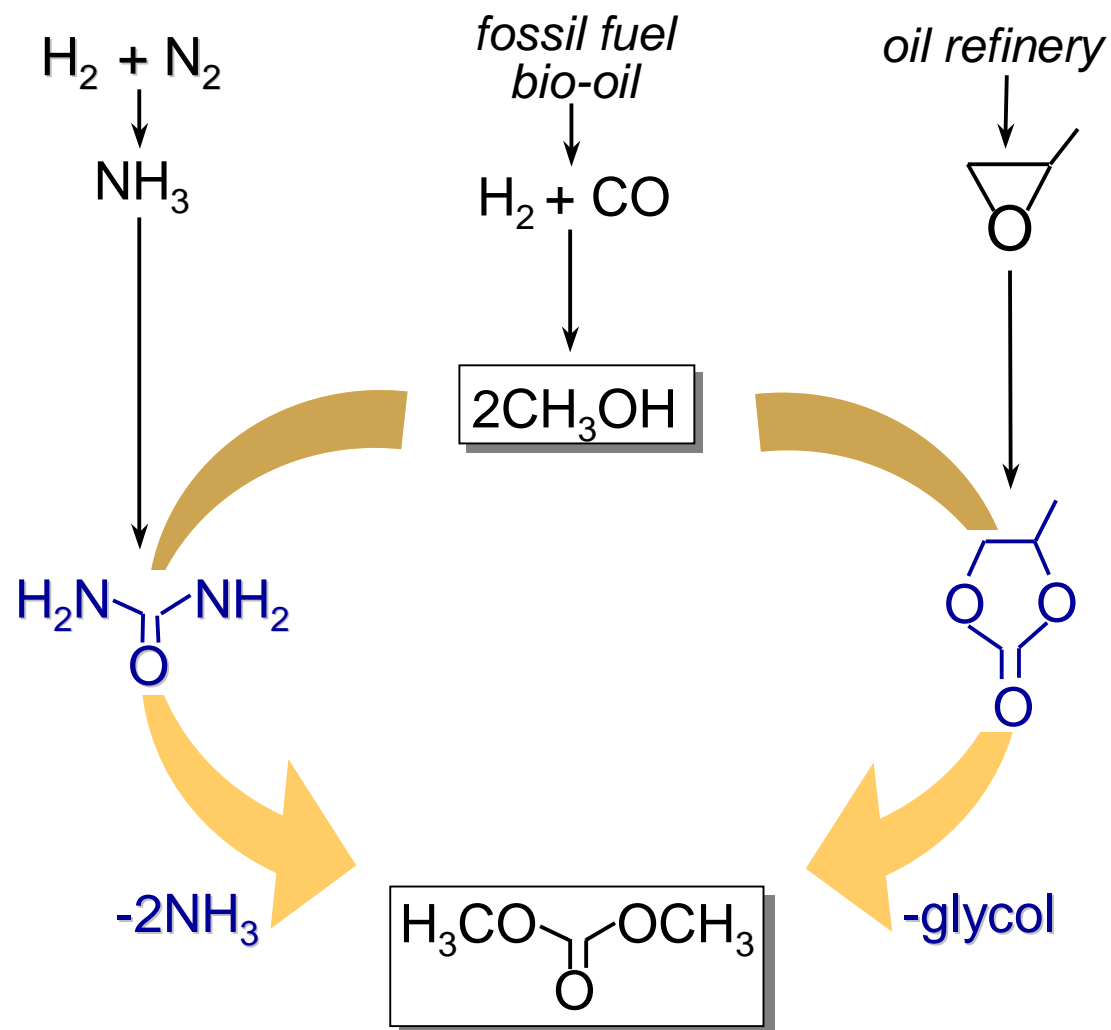


0.1 Mt/y

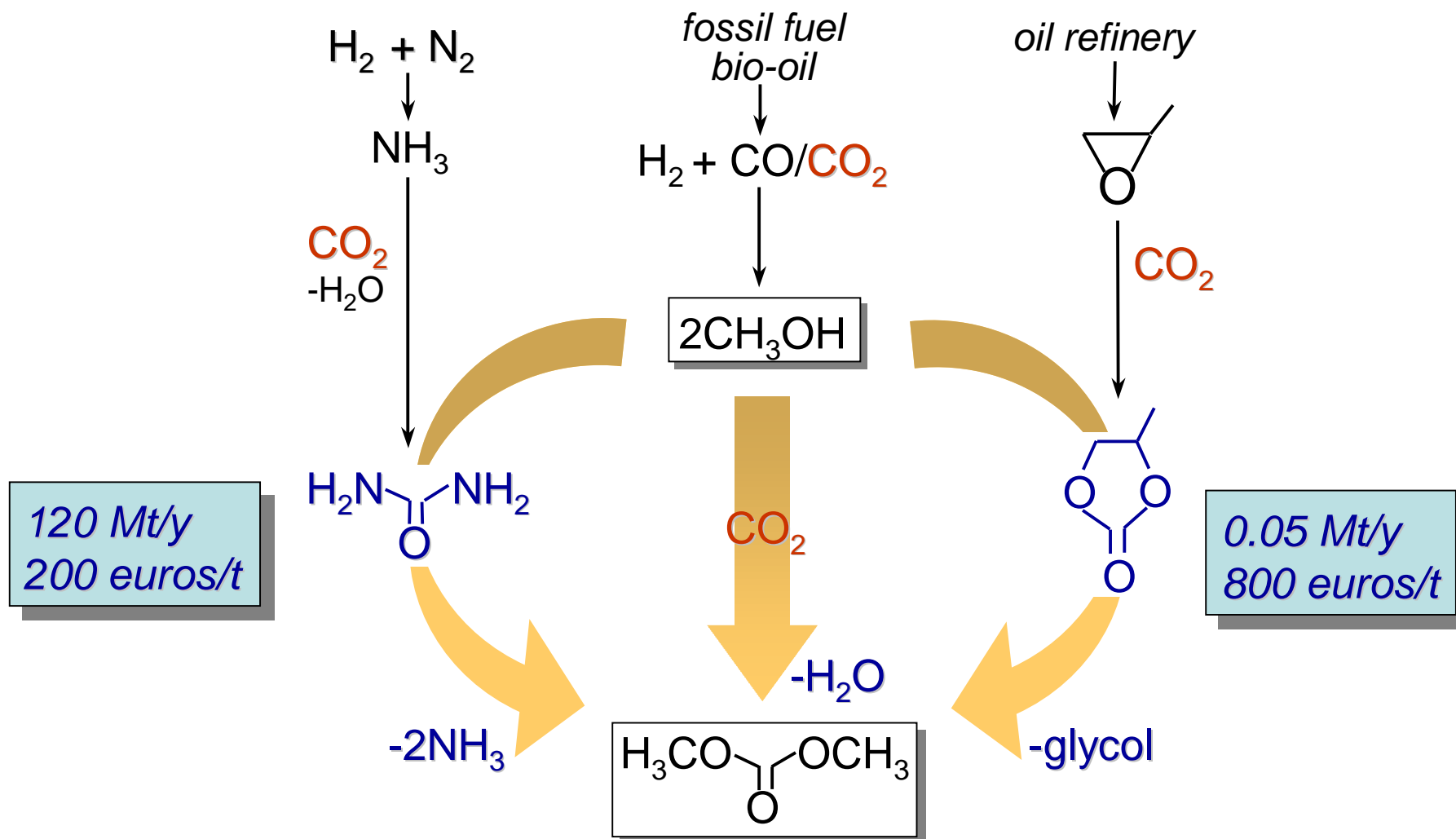
≈ Mt/y



CO₂ routes to dialkyl carbonates

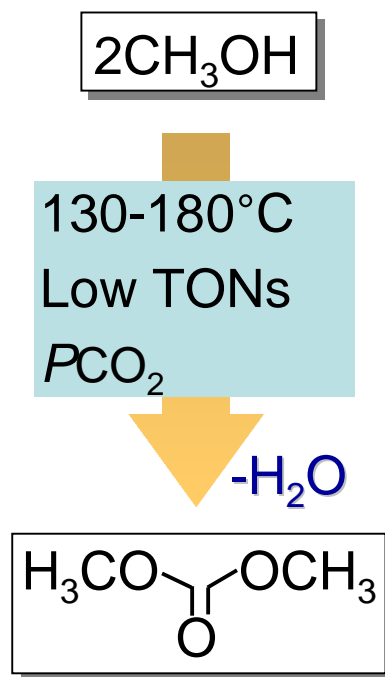


CO₂ routes to dialkyl carbonates



Catalysts

- ZrO_2
- $\text{R}_2\text{Sn}(\text{OCH}_3)_2$



- Issues

- Identify the factors responsible for low TONs
- Rationalize pressure effect

- Mechanism
- Fluid phase equilibria
- 2nd generation catalysts

J. Kizlink, 1993
Patent to RWE, 1994
T. Sakakura, 1999
K. Tomishige, 1999
D. Ballivet-Tkatchenko, 2000

Co-operation

- Organometallic chemistry

Prof. H. Chermette (Villeurbanne)
Prof. E. Dinjus (FZK-Karlsruhe)
Dr. G. Laurenczy (EPFL, Lausanne)

- Catalysis

- Process engineering

- Environmental engineering

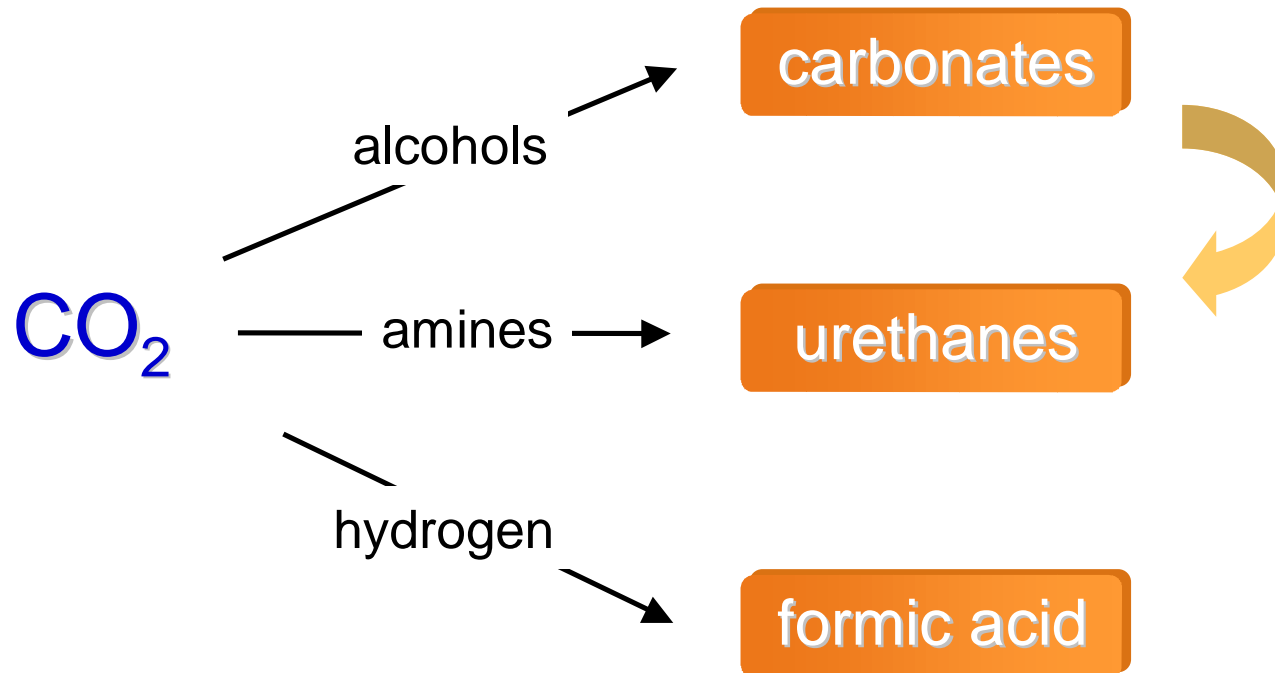
Univ. Oulu

Prof. R. Keiski, Dr. E. Pongracz

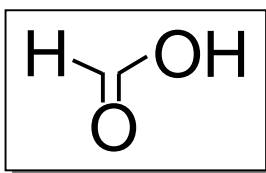
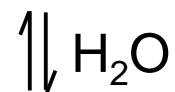
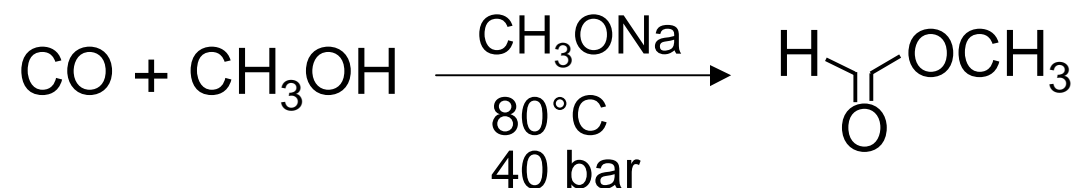
Åbo Akademi

Dr. J.-P. Mikkola

CO₂ vs CO-based technologies

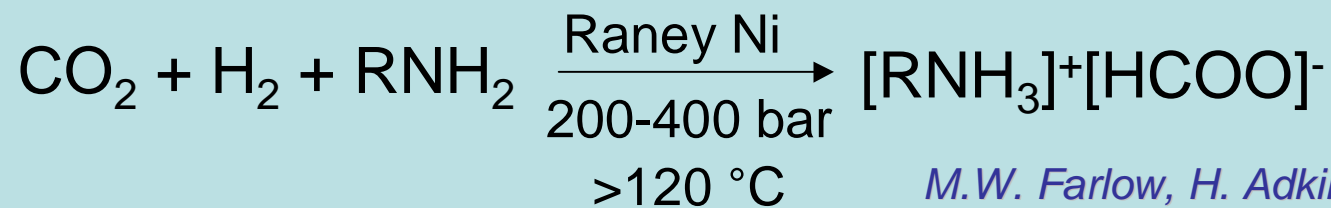


Formic acid synthesis



Commodity
chemicals

Polymers



M.W. Farlow, H. Adkins, 1935

CO₂ to formic acid

- Organometallic catalysts Ru, Pd, Rh

$T \ll 100^\circ\text{C}$, $P < 200$ bar

TONs 100

2000

5000

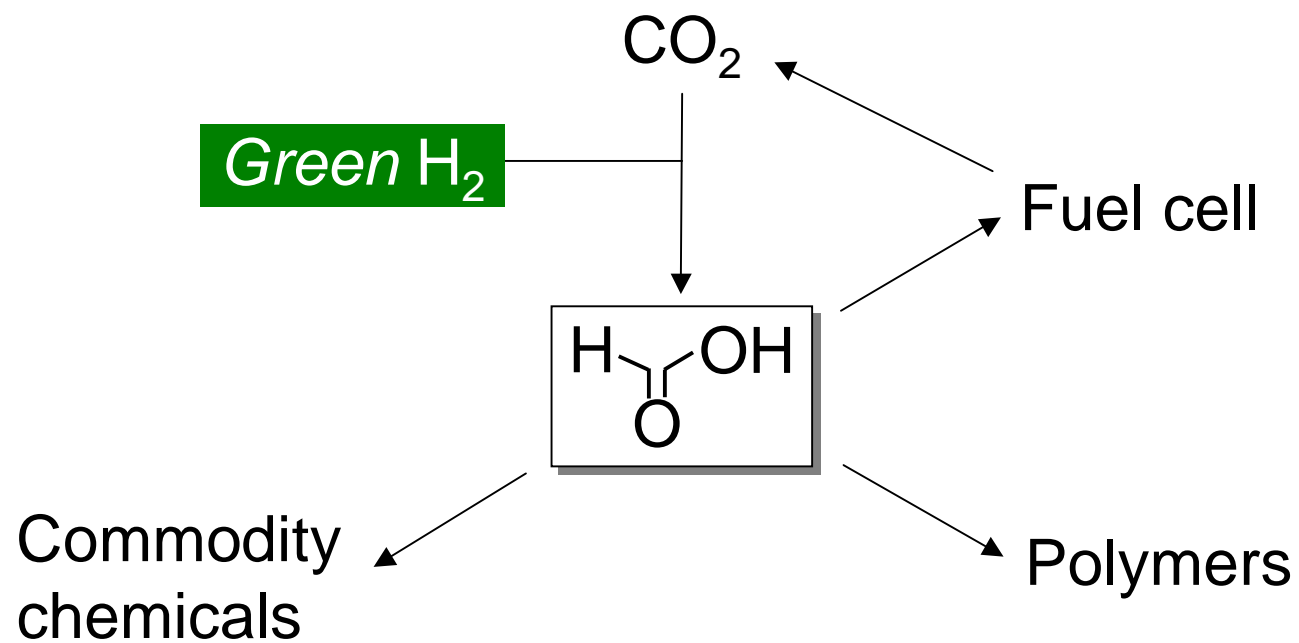
420 000

TOF 95 000 h⁻¹

- TONs & TOFs extremely sensitive to reaction conditions
- Mechanism

Y. Inoue, 1976; E. Dinjus, Ph. Jessop, W. Leitner, R. Noyori, 1994; A. Baiker, 1997; A. Behr, 2004; Ph. Jessop, 2002; A. Baiker, 2007

CO₂ to formic acid



Technology shifts

- CO₂ greener than organic solvents
- CO₂ safer than phosgene
- CO₂ + H₂
to formic acid
to methanol
- CO₂ + CH₄
to acetic acid
- For a recent review
T. Sakakura, J.-C. Choi, H. Yasuda
Chemical Reviews, **2007**, *107*, 2365

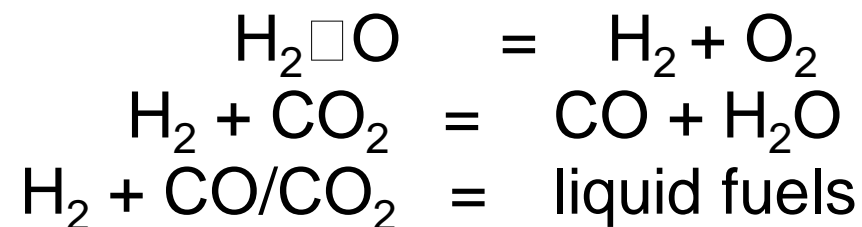
Economics less costly
than global warming issues

Outlook

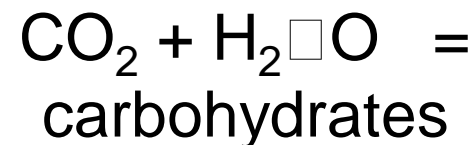
Hydrocarbons for ever?

New Chemistry

long term



more diverse feedstocks



Metal-Oxygen bonds
Metal-Carbon bonds