Long Term Sustainability through Carbon Dioxide Capture and Conversion: The Methanol Economy

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Increasing world population
Increase in standard of living

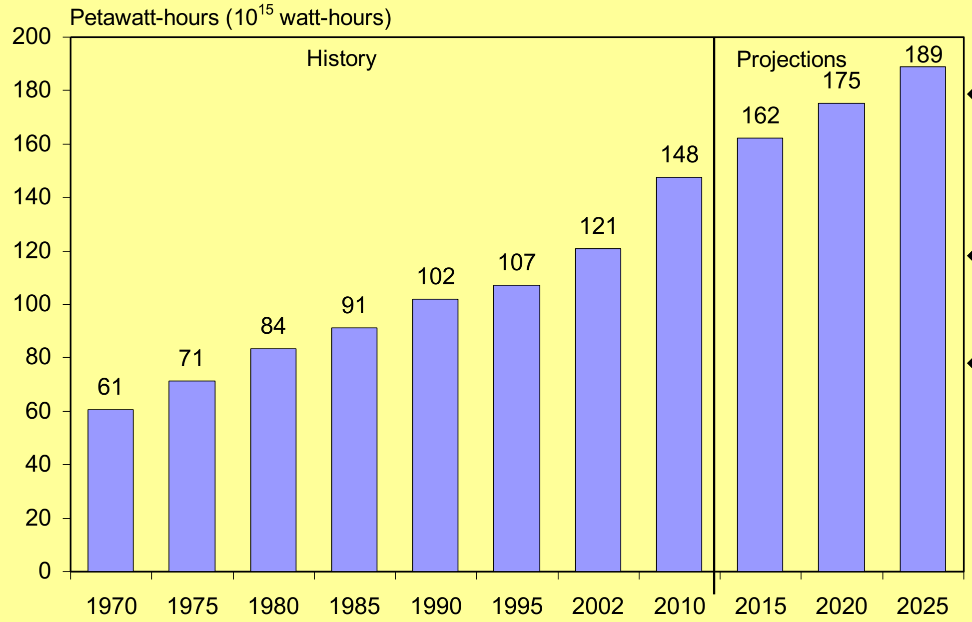
Increase in fossil fuel use
-Oil, gas, coal (hydrocarbons)
Finite sources – non-renewable
On the human timescale

Increase in carbon dioxide content of the atmosphere
Greenhouse effect
(Global warming).~ 415 ppm

World population
(in millions)

1650	1750	1800	1850	1900	1952	2000	2011	Projection 2050*
545	728	906	1171	1608	2409	6200	7000	8000 to 11000

* Medium estimate. Source: United Nations, Population Division

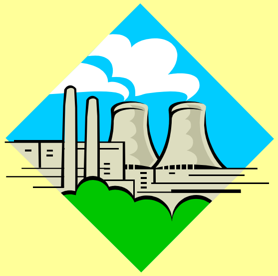


World Primary Energy Consumption, 1970 to 2025

Based on data from Energy information Administration (EIA)

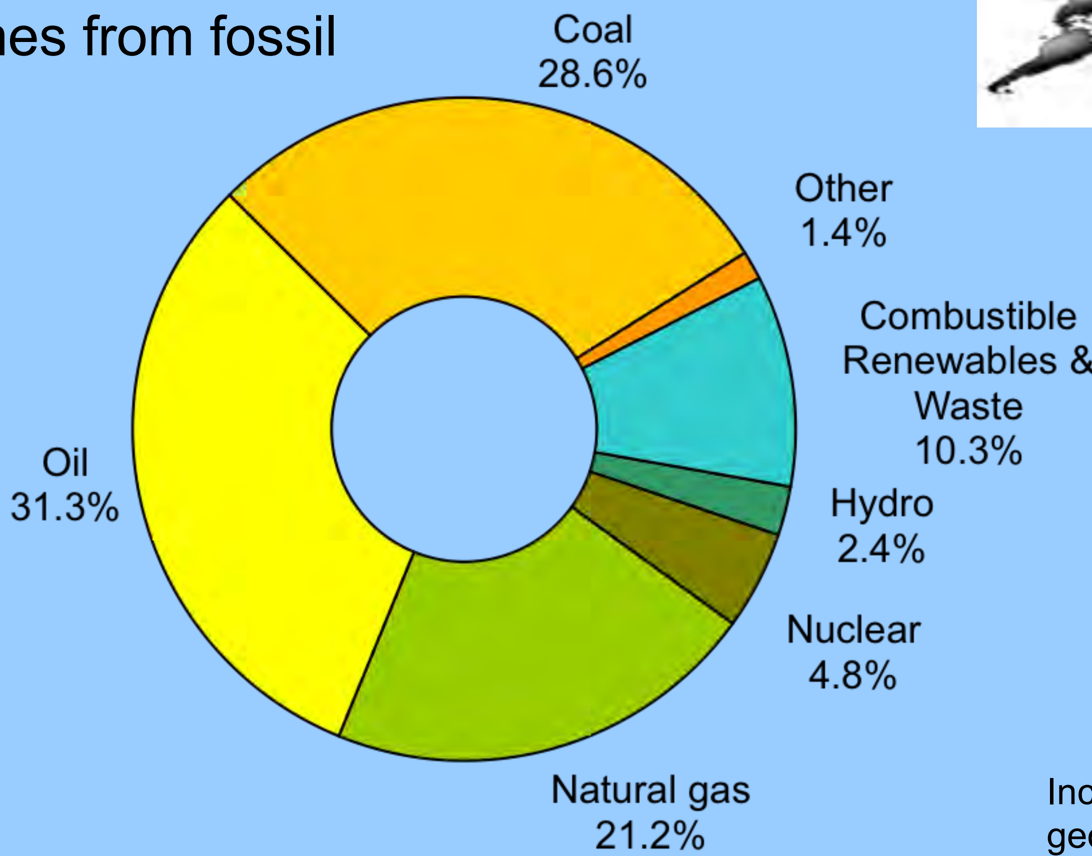
- ❖ **180 petawatt-hours ~ 18 terawatts (18,000 power plants of 1 gigawatt)**
- ❖ **21 TW by 2025**
- ❖ **30 TW by 2050**

30000 X



Distribution of the World Total Primary Energy Supply in 2014

More than 80% of our energy comes from fossil fuels!



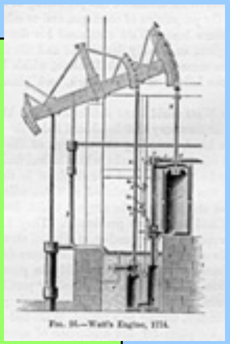
Includes solar, wind, geothermal, ocean energy

Total 13 699 Mtoe

Based on data from the International Energy Agency (IEA) Key World Energy Statistics 2016

Hydrocarbon Sources

17^{th}-19th Century - industrial revolution **coal**

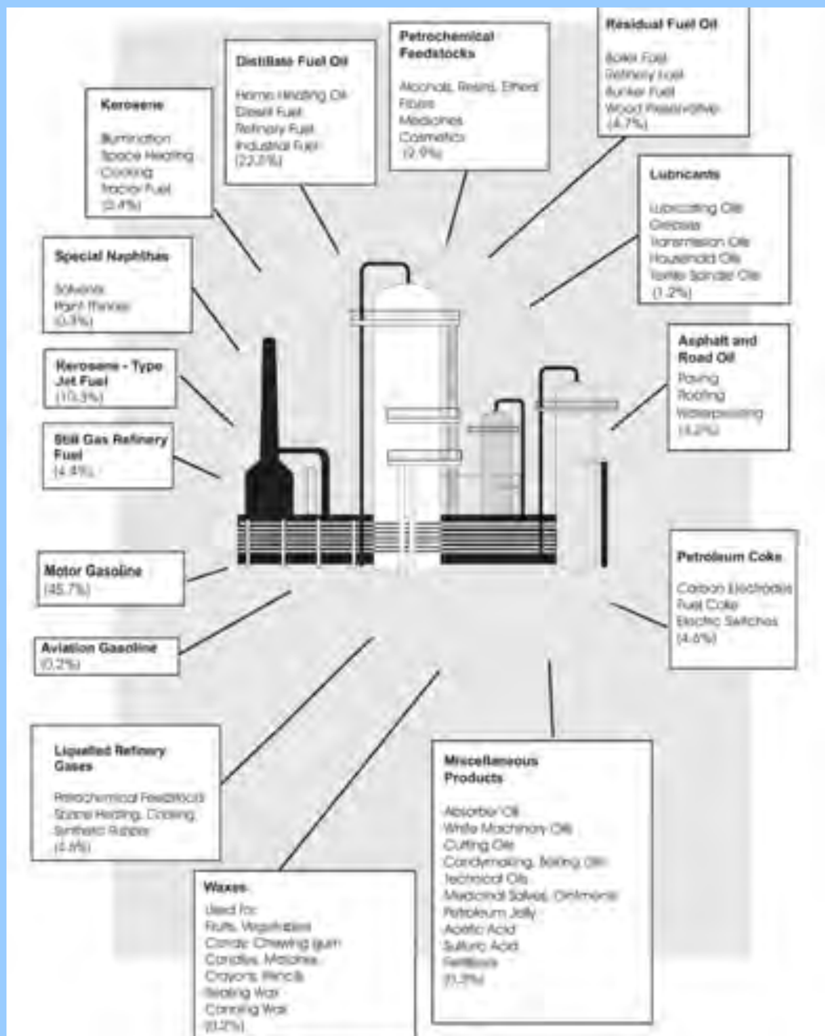


19^{th} Century **coal, oil**

20^{th} Century **coal, oil, natural gas**
(fossil fuels)

21^{st} Century **fossil fuels**
carbon dioxide

Dependence on petroleum and other fossil fuel products as chemical feedstock



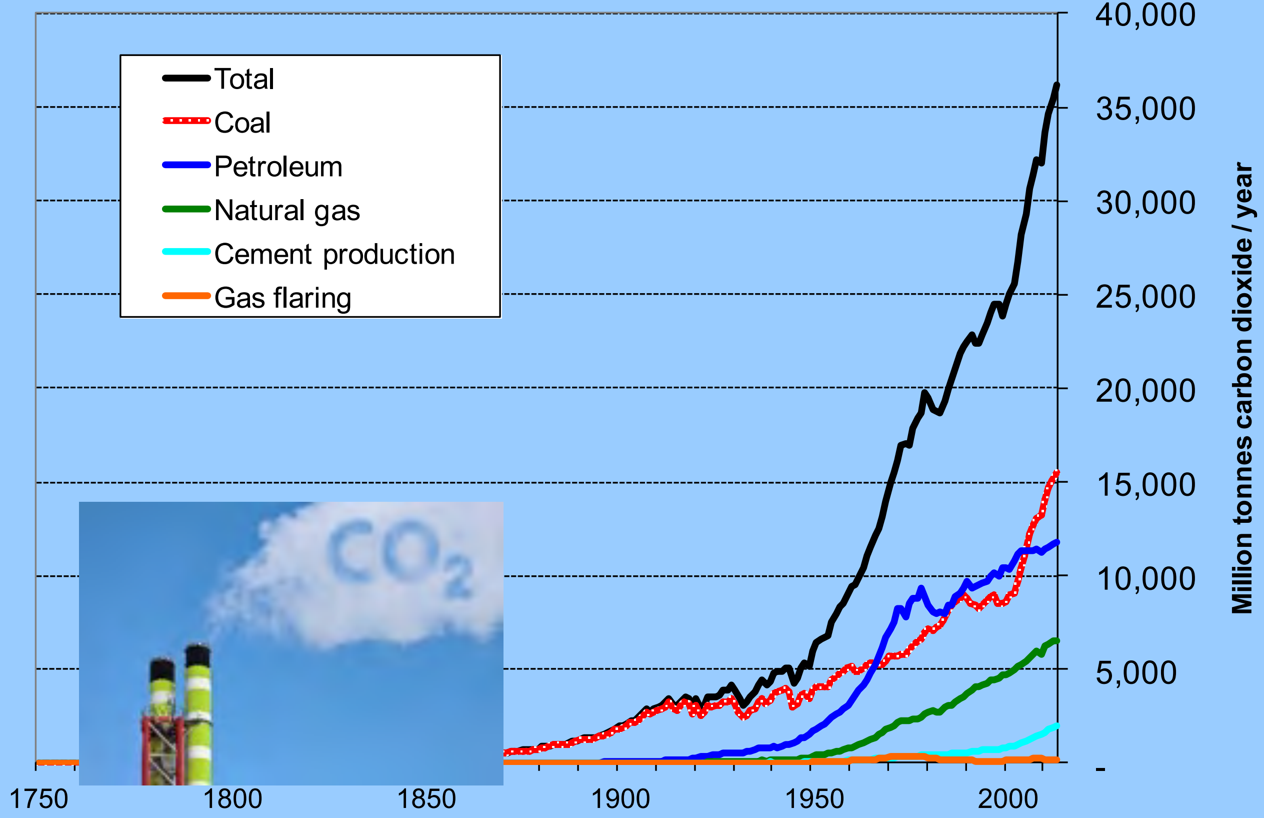
In United States **67%** of the petroleum currently used in transportation as gasoline, diesel, jet fuel, etc.!

Transportation sector utterly dependant on petroleum oil (>90%)

About 5-10% of petroleum also provide a vast number of essential products such as plastics, fertilizers, medicines, etc.

➡ Beside CO_2 emissions, fossil fuels are also finite, non-renewable and therefore unsustainable in the long run

Annual global CO_2 emissions – 1750-2013

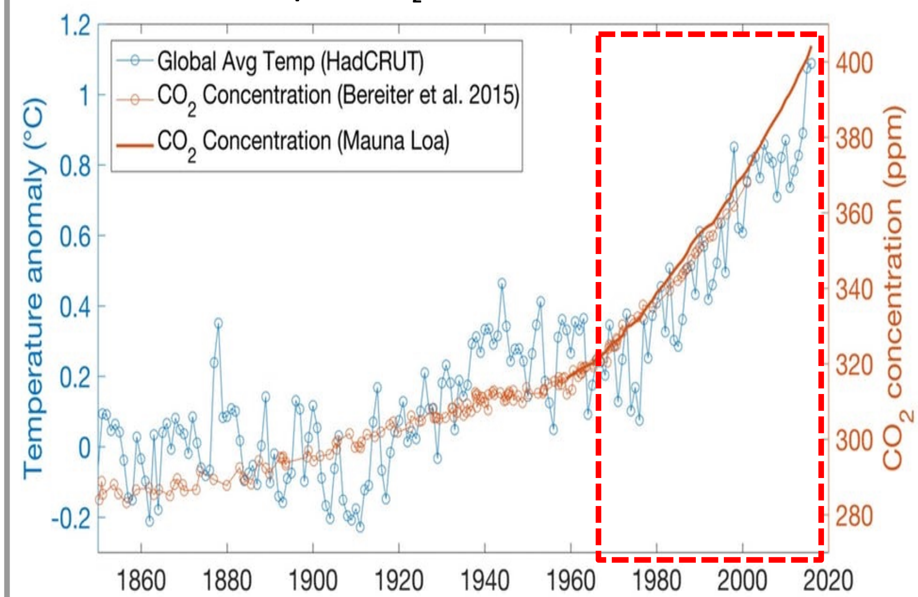


More than 35 billion tonnes of CO_2 released into the atmosphere in 2013 and in 2017, it was 40 billion tonnes.

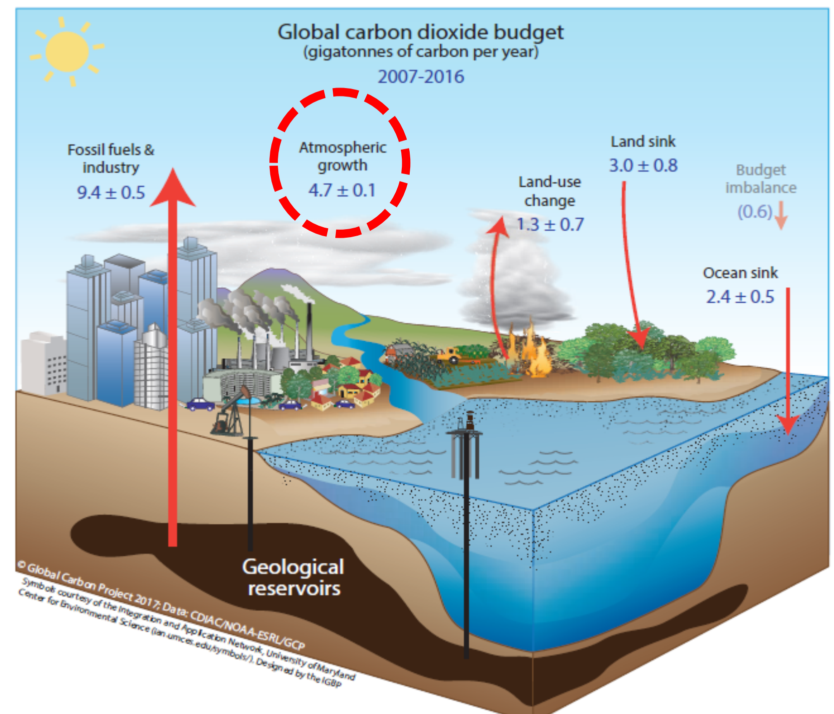
About half the CO_2 emissions accumulate in the atmosphere. Presently more than 20 billion tonnes per year, contributing to **global warming**, **glacier ice melting- sea level rising** and **climate change**. Dissolution in the ocean results in **ocean acidification** and **destruction of coral reefs**!

The Carbon Dioxide Conundrum

Global Temperature Anomaly and Atmospheric CO_2 concentration since 1850.



Source: http://www.climatecentral.org



C. Le Quéré et al.: Global Carbon Budget 2017

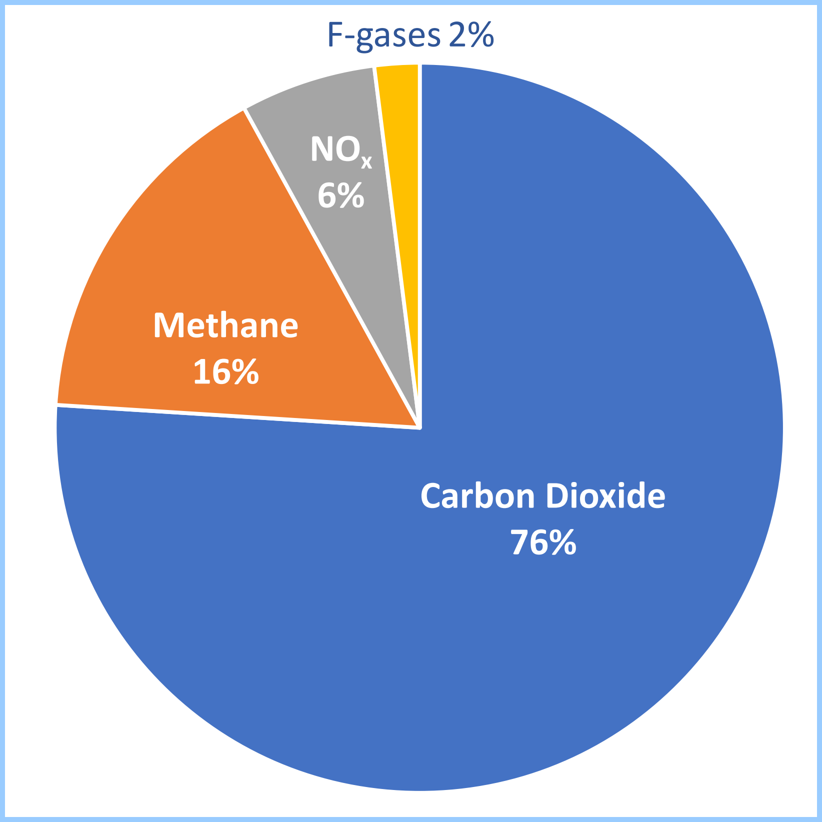
~ 55% rise in CO_2 concentration from pre-industrial age!

Latest CO_2 Reading: **413.65 ppm** (Aug 3 2020)
Highest CO_2 Reading: **418.32 ppm** (Jun 1 2020)

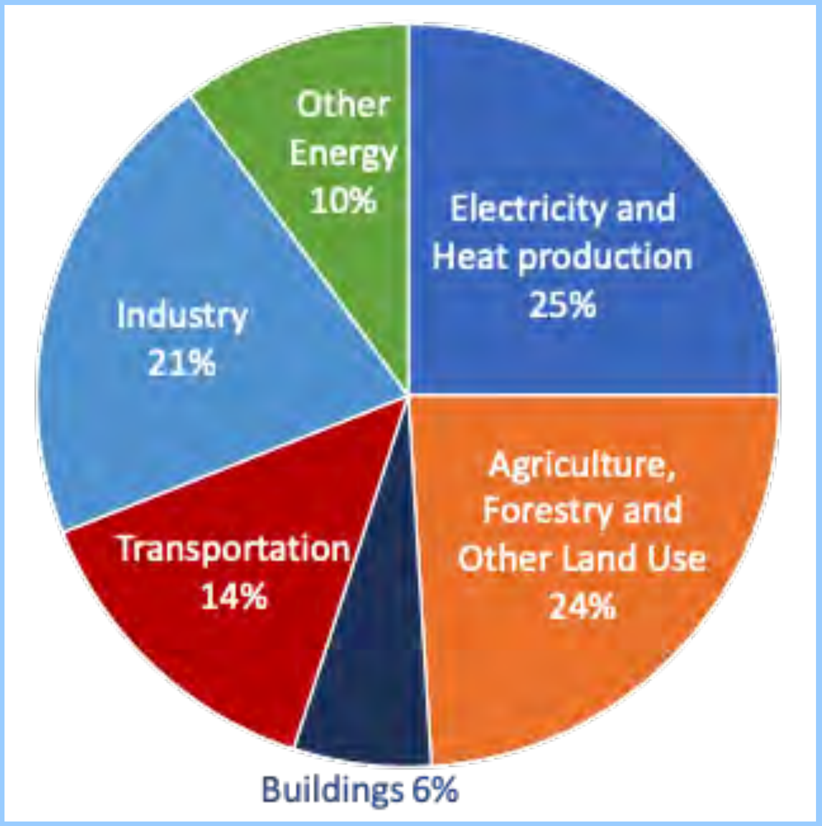
Source: Earth System Research Laboratory, NOAA, Mauna Loa Observatory

Anthropogenic Greenhouse Gas Emissions

Global Greenhouse Gas Emissions

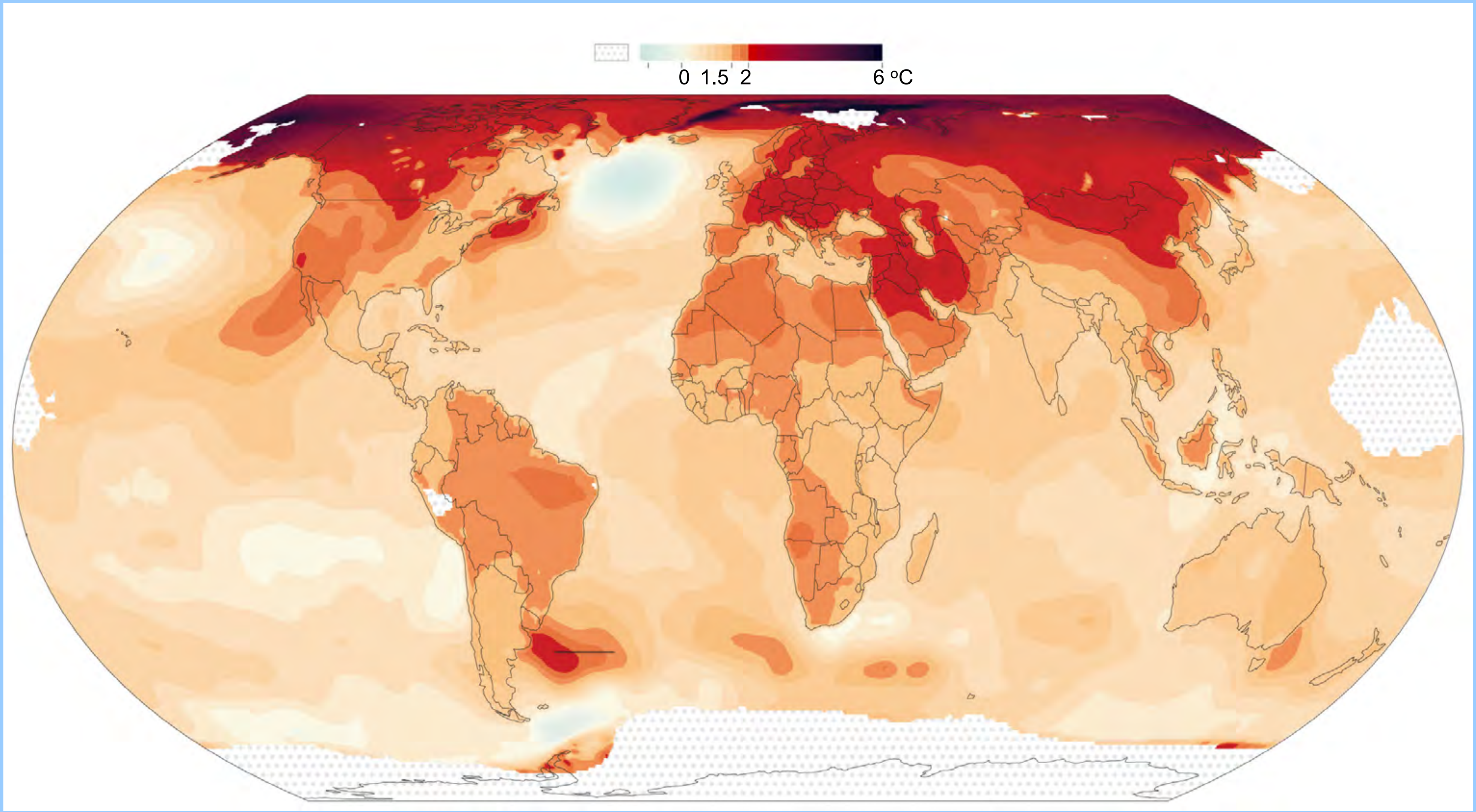


Global Greenhouse Gas Emissions by Economic Sector



Source*: IPCC, 2014: Climate Change 2014: Mitigation of Climate Change.*

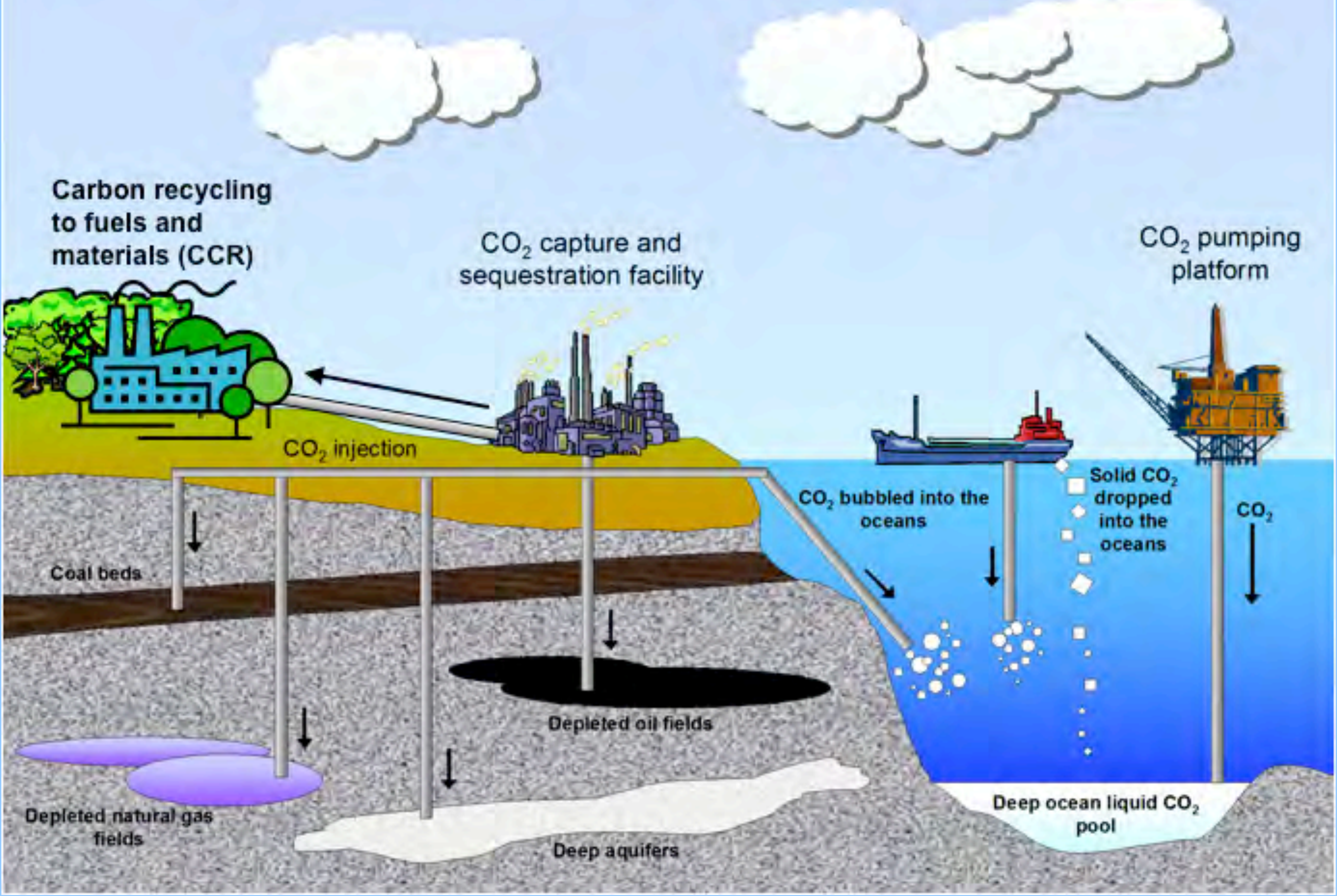
Global Temperature Change, 2014-2018 compared with 1180-1899

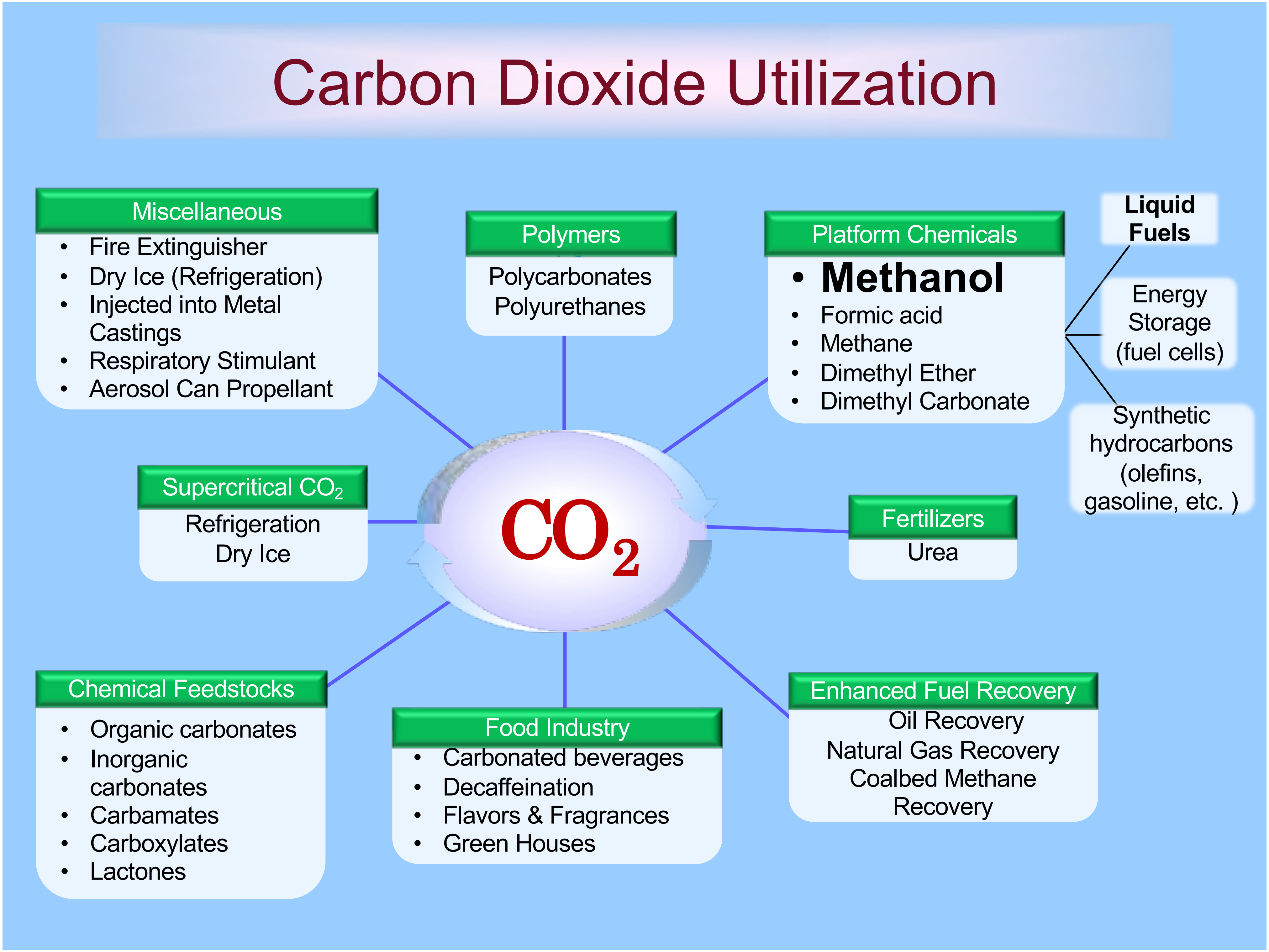


The fastest-warming zones include the Arctic, much of the Middle East, Europe and northern Asia, and key expanses of ocean. A large part of Canada is at 2 °C or higher.

Washington Post, September 11, 2019

Carbon capture and sequestration (CCS)




Carbon Dioxide Utilization
Miscellaneous
• Fire Extinguisher
• Dry Ice (Refrigeration)
• Injected into Metal Castings
• Respiratory Stimulant
• Aerosol Can Propellant
Polymers
Polycarbonates
Polyurethanes
Platform Chemicals
• Methanol
• Formic acid
• Methane
• Dimethyl Ether
• Dimethyl Carbonate
Liquid Fuels
Energy Storage (fuel cells)
Synthetic hydrocarbons (olefins, gasoline, etc.)
Supercritical CO_2
Refrigeration
Dry Ice
CO_2
Fertilizers
Urea
Chemical Feedstocks
• Organic carbonates
• Inorganic carbonates
• Carbamates
• Carboxylates
• Lactones
Food Industry
• Carbonated beverages
• Decaffeination
• Flavors & Fragrances
• Green Houses
Enhanced Fuel Recovery
Oil Recovery
Natural Gas Recovery
Coalbed Methane Recovery

Daily usage of fossil fuels

- ❖95 Million Barrels of Oil is consumed!
- ❖10 Billion m^3 of Natural Gas
- ❖16 Million Tonnes of Coal

> 40 billion tonnes of CO_2 released into the atmosphere per year
Contributing to greenhouse effect – Global Warming

Ethanol economy: in the US, 13. 9 billion gallons of ethanol is produced per year (~330 million barrels) from corn. Equivalent to 225 million barrels of oil: 2.5 days supply!

In Brazil, 5.57 billion gallons of ethanol from sugar cane is produced.

Biodiesel a lot smaller: requires more land.

Biomass

CO_2 fixation by photosynthesis (carbon neutral)

$$nCO_2 + nH_2O \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} n(CH_2O) + nO_2$$

Biofuels- Ethanol, Butanol, Vegetable Oils (Biodiesel)- a small % of the energy mix.

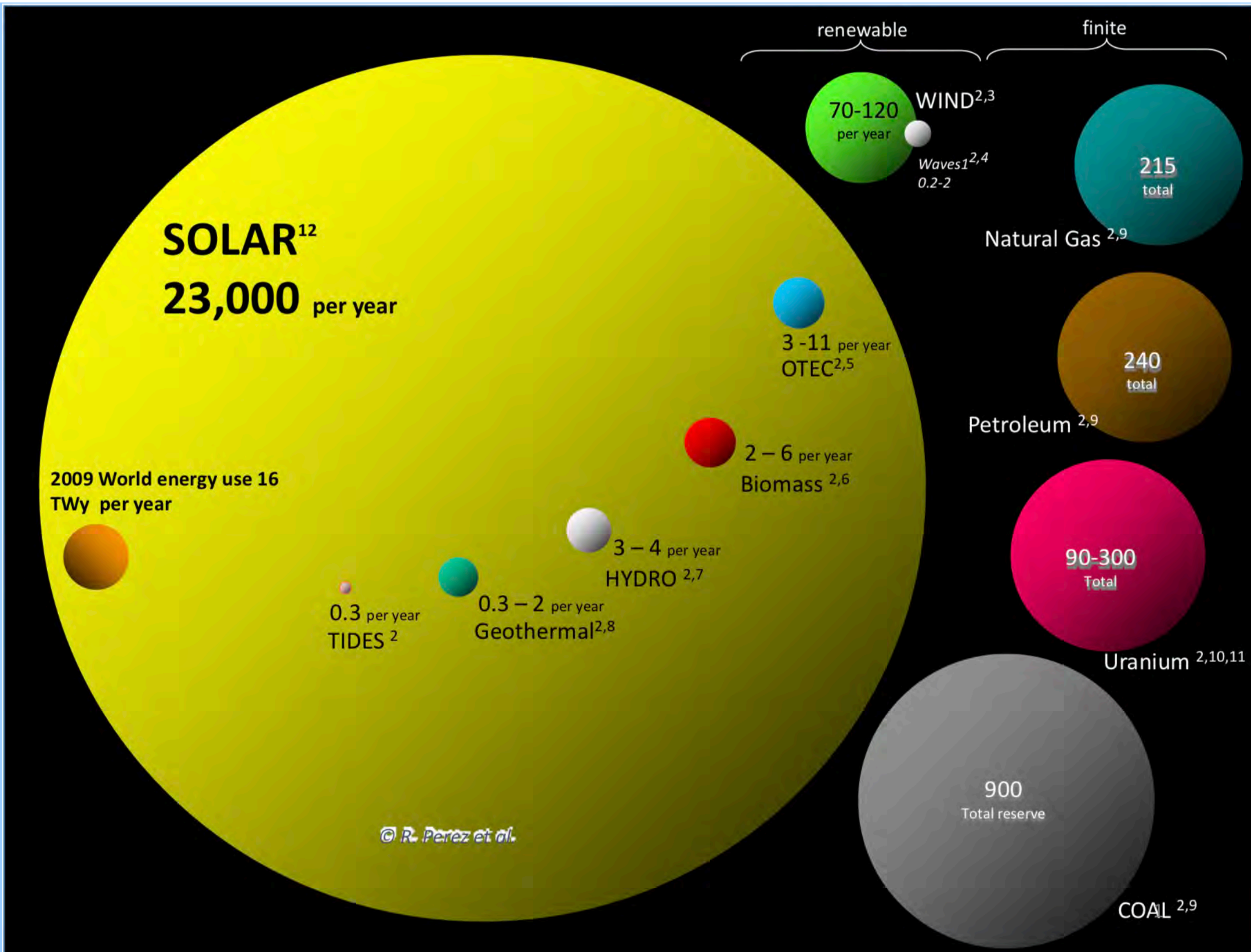
- Land availability and use
- Water resources- Irrigation

* Food security vs Energy security

- Fertilzer use (nitrogen fertilizers from NH_3 (N_2 and H_2 (syngas)- Haber- Bosch Process)
- Processing technologies, energy use

* Overall energy balance and life cycle

Sun is the source of most energy on Earth- past, present and future 23,000 TWy per year- A reliable nuclear fusion reactor!



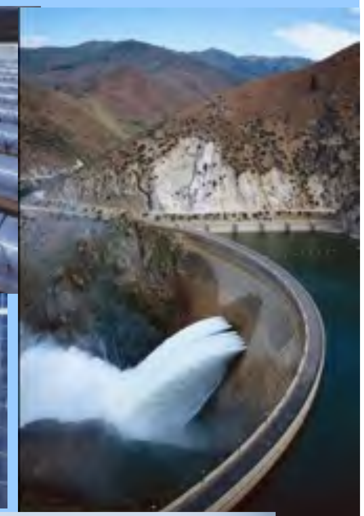
2009 Estimate of finite and renewable planetary energy reserves (Terawatt-years). Total recoverable reserves are shown for the finite resources. Yearly potential is shown for the renewables.

Marc Perez and Richard Perez IEA-SHCP-Newsletter Vol. 62, Nov. 2015

What are the issues? Why not use more alternative energies and resources?

Hydropower
Geothermal energy
Wind energy
Solar energy
Biomass
Ocean energy (waves, tides, thermal)
Nuclear energy





Why don't we use more alternative energies? -
Mainly a problem of cost (improving rapidly)
- Fossil fuels are still the biggest bargain nature ever gave us
- The most promising (solar, wind) are intermittent and fluctuating
-They produce mostly electricity
-Battey technology has not advanced


Hydrogen Economy

Hydrogen economy (clean fuels, fuel cells)

- Hydrogen is not a primary energy carrier, b.p. = -253 °C
- Tied up in water and fossil fuels
- Incompatible with 20% oxygen in the air
- Liquid hydrogen has 1/3 Volumetric energy density of gasoline
- 2 grams occupy 22.4 liters of volume at NTP (high pressurization is required)
- Infrastructure is very expensive (hydrogen diffuses easily)
- Highly flammable (colorless flame)

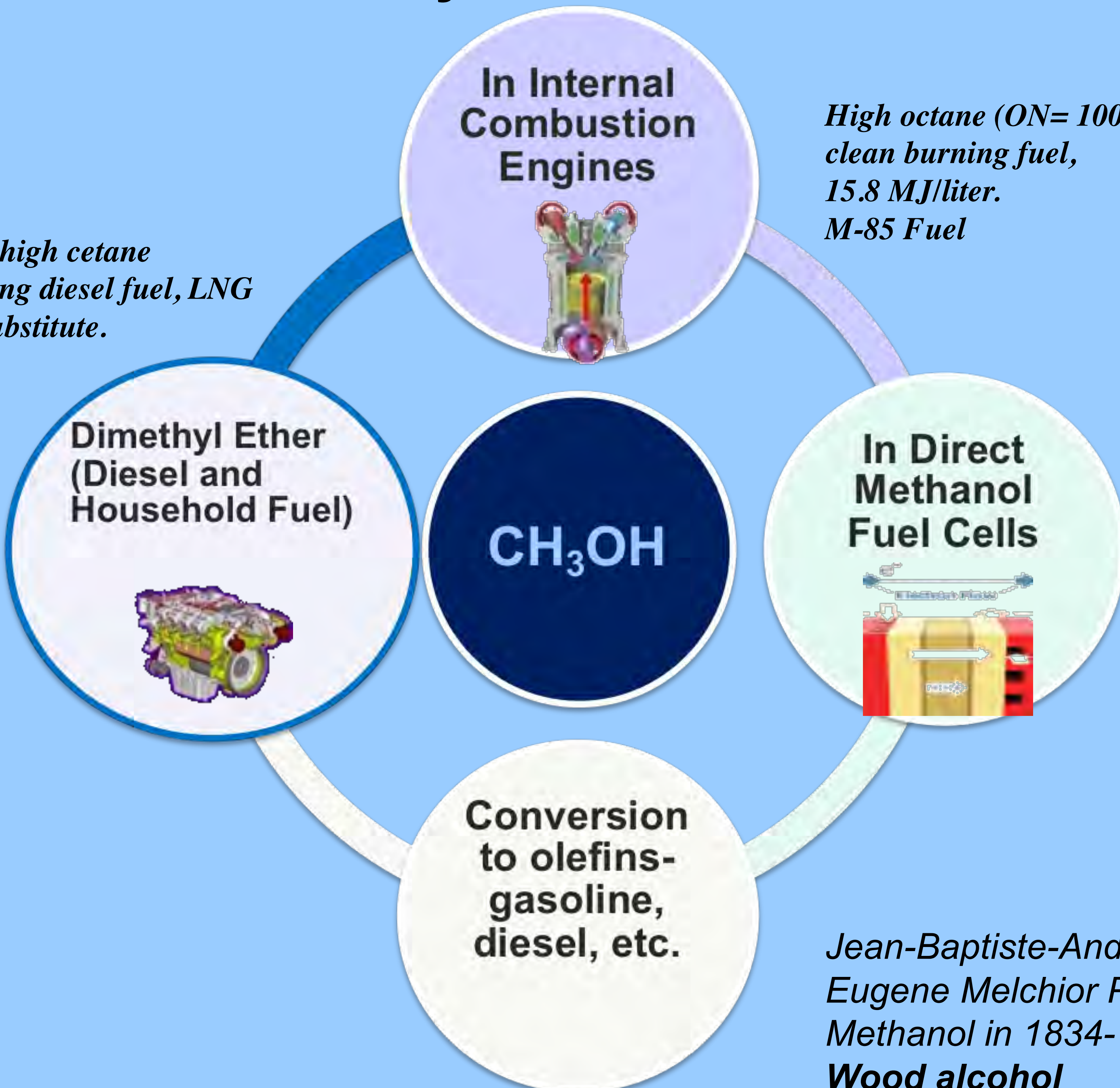
The Methanol Economy

The late Professor George A. Olah (1927- 2017)
1994 Nobel Laureate in Chemistry
A Major Proponent of the Methanol Economy Concept

The Methanol Economy: Methanol as a fuel and feed-stock

CH_3OCH_3, high cetane clean burning diesel fuel, LNG and LPG substitute.

High octane (ON= 100) clean burning fuel, 15.8 MJ/liter. M-85 Fuel



*Jean-Baptiste-Andre Dumas and Eugene Melchior Peligot isolated Methanol in 1834- **Wood Spirit, Wood alcohol***

Methanol properties

❖Methanol (methyl alcohol, wood alcohol) is an excellent internal combustion engine/turbine fuel- It is a liquid (b.p 64.7 ^oC).

❖Methanol has a high octane number (~ 100)- used in Race cars.

❖M85- used in Flex-Fuel vehicles (similar to E-85).

❖Half the volumetric energy content of gasoline (15.8 MJ/liter), but more efficient and cleaner burning.

❖Methanol can be blended into Biodiesel (Esterification). Converted to dimethyl ether and dimethyl carbonate.

❖Methanol is an excellent hydrogen carrier -easily reformed to H_2 (syngas) at modest temperatures.

Drawbacks

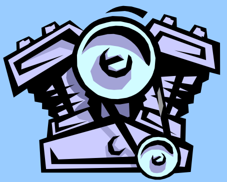
❖ Methanol is miscible in water - corrosive for Al, Zn, Mg
Solution: use compatible materials - Flexfuel vehicles

❖ Methanol has low vapor pressure at low temperatures
Solution: spike it with gasoline- M85 (M15, M5)

❖ Ingestion > 20 mL can be lethal - Dispensing should not be a problem

❖ Spillage - very safe to the environment
methanol used in water treatment plants for denitrification

Methanol in ICE



- ❖ Octane number 100- fuel/air mixture can be compressed to smaller volume-results in higher compression ratio
- ❖ Methanol has also has higher "flame speed"- higher efficiency
- ❖ Higher latent heat of vaporization (3.7 times higher than gasoline)- can absorb heat better - removes heat from the engine- air cooled engines. Can be blended with gasoline in various ratio (M5, M10, M15, M85 up to M100)
- ❖GEM fuels, gasoline/ethanol/methanol also possible (Lotus)
- ❖Methanol burns better- cleaner emissions; less NO_x and PM
- ❖ Safer fuel in fires than gasoline
- ❖Methanol is a liquid which can be dispensed in regular gas station requiring only limited modifications (unlike H_2)
- ❖Compatible with hybrid (fuel/electric) systems

Race car

Taxi fleet in China

Buses in China

Various Road Transport Options

M3 – M15

- EU allows M3 (EN228)
  Blended a.o. in UK and NL
- China uses M15
  Estimated 7 million metric tons
  ~75% of cars built by international automakers
- Trials in Australia, Israel, a.o.

A20 – A30

- Automakers call for higher octane to facilitate greater engine efficiency *(higher compression, turbocharging, downsizing)*
- Methanol and ethanol alcohol fuels together at mid-level blends provide needed octane

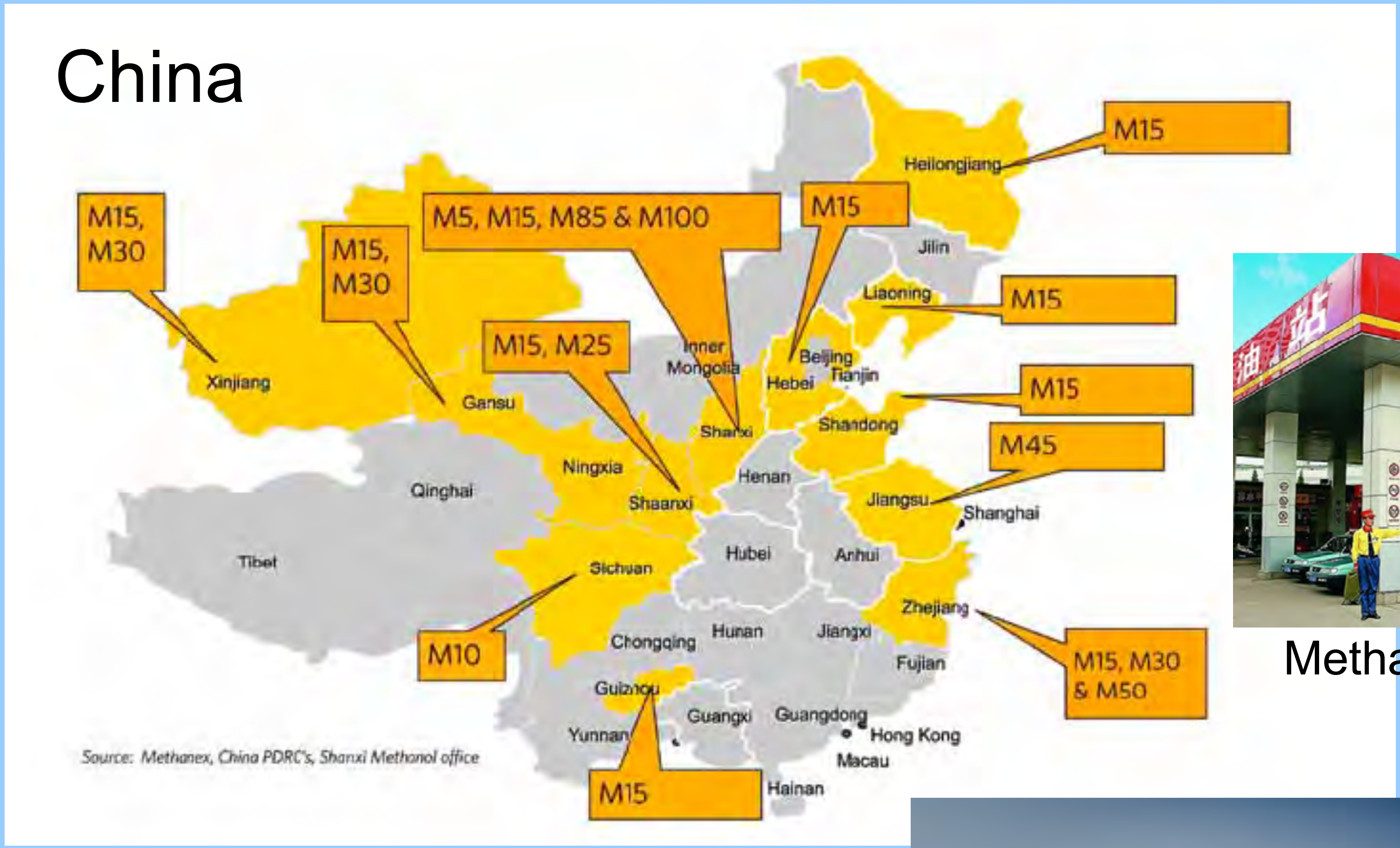
M51-100

- ASTM D5797 standard revision
- M100 dedicated vehicles *(e.g. Geely)*
- Use of SI technologies in Light and Heavy Duty vehicles
- Few changes needed to existing vehicle technologies at low cost

China High Proportion Methanol Fuel

2009	2012	2016	180,000
China adopted national standards for M85 and M100	MIIT "high proportion" methanol demonstration to serve as the basis for M85 vehicle standards in Shanxi, Shaanxi, and Shanghai, and has expanded to other provinces and cities	7 million tons (2.3 billion gallons/8.7 billion liters) of methanol blended with gasoline, against total gasoline consumption of 2.25 million barrels per day or 34.5 billion gallons/130 billion liters	Vehicles converted to methanol fuel, mostly taxis

Methanol blending around the world



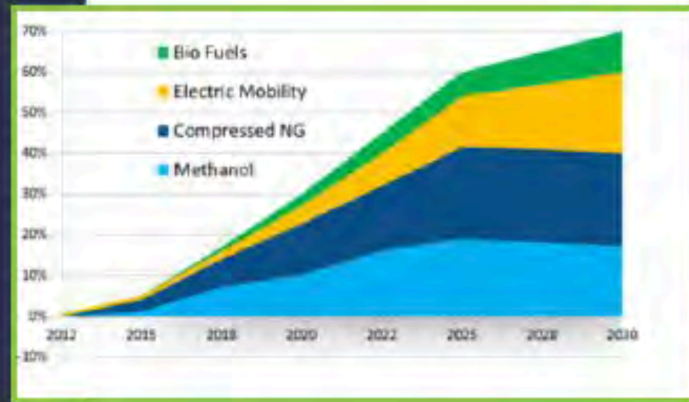
Methanol filing station

Israel


一汽解放锡柴
造每个人的精品车
吉利汽车
甲醇新能源汽车
GEELY

Israel Methanol Fuels Demonstrations

- Israel fundamentals:
  - Large gas finds in Israel
  - Strategic need to reduce oil dependence
- Prime Minister Netanyahu established Fuel Choices Initiative.
- Driven 1,000,000 kms on M15 fuels with improved power and torque.
- In 2016, Israel adopted national standard for M15 fuels.
- Fiat marketing M15 car in Israel, and Dor Chemicals has introduced M15 retails pumps



India: Roadmap to Methanol Economy

- **On 11 September 2015, NITI Aayog held brainstorming session on possible roadmap for Methanol Economy for India's long-term energy security**
- **Formed three Expert Groups:**
  - Production of Methanol and DME
  - Utilization of Methanol and DME
  - Research and Development
- **The Methanol Institute has committed to assisting the Expert Groups as they look to opportunities to increase methanol production from coal and biomass, and utilize methanol and DME as transportation fuels**
- **MI jointly organized Methanol Economy International Seminar held in Delhi on 6-7 September 2016**

GENSET METHANOL CONVERSION

MODIFICATIONS:

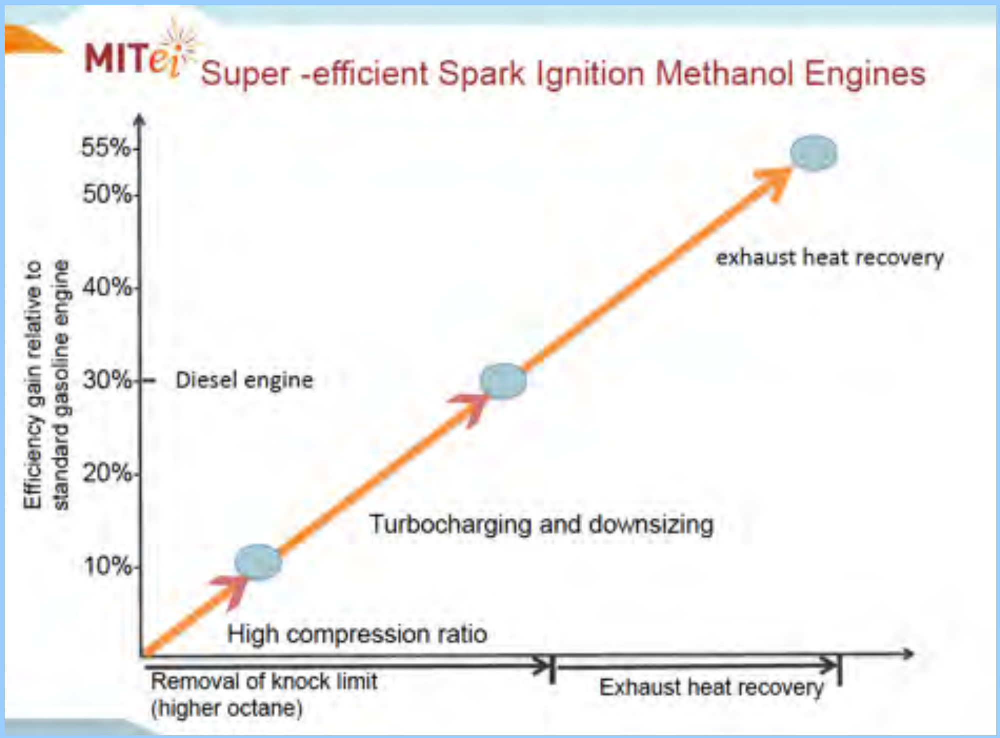
- Combustion Chamber
- Carburettor

Diesel-like efficiency and torque with methanol (Daniel Cohn-MIT)

• Methanol provides exceptionally strong suppression of engine knock, especially when it is directly injected

• Higher allowed turbocharging pressure than gasoline or natural gas

• Spark ignition methanol engine could provide around 1.5 X more torque/liter than diesel



Potential Spark Ignition Methanol Operation In Modified Diesel Engine (e.g 9 Liter engine)

	Engine type		
	Diesel	Methanol	Diesel
Engine size (Liter)	9	9	15
Torque (lb-ft)	1300	2000	2000

Professor Chunde Yao, Professor, State Key Laboratory of Engines, Tianjin University

Marine Fuel in Transition

•Bunker fuel – usually made from diesel has been historically used in the shipping industry.

•With over 90,000 commercial vessels moving around the world's oceans, shipping consumes 370 million tons of fuel (Heavy Fuel Oil and Middle Distillates).

•Bunker fuel has been highly polluting; high SOx, NOx, particulate emissions.

Methanol as a marine fuel in diesel engines

Methanol much cleaner than diesel fuel (PM, SO_x, NO_x)

Emission control area (ECA) in the North Sea and Baltic Sea

Environment and cost benefit for methanol

→ In this case regulation actually helped fuel methanol

Level of SO_x set at 0.1% max since 2015

Relatively easy conversion of diesel engines to methanol operation

Methanex methanol powered tanker

Ferry Stena Germanica's conversion to methanol power was a world first!

Göteborg-Kiel line

4 Wärtsilä engine with a total of 32,000 horsepower!

Retrofitting of Wärtsilä marine engine

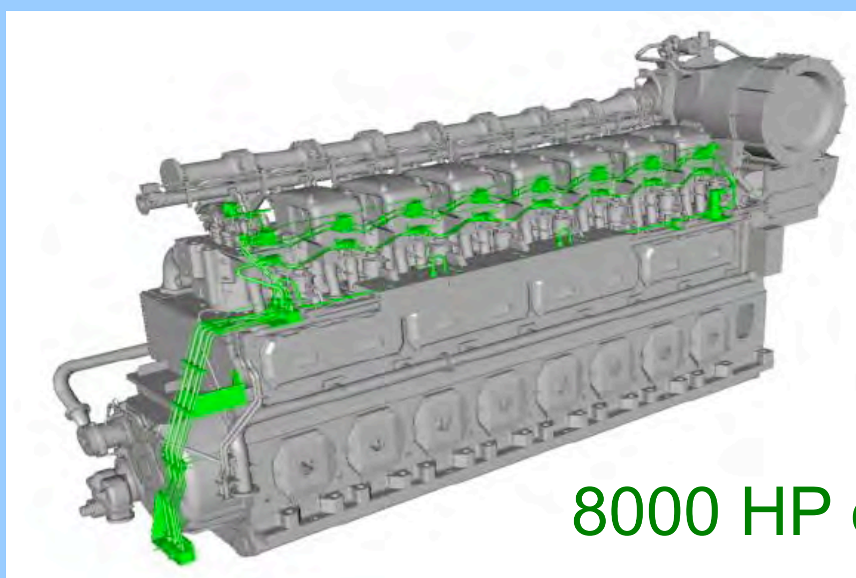
Only minor modifications needed for engine retrofitting to methanol fuel. Mainly fuel delivery system

Hydrid system: methanol or diesel can be selected in a fast and reliable way without having to stop the engine and without losses in power output

Engine before and after conversion

before **after**

Higher efficiency in methanol mode



8000 HP engine (6000 kW)

Dimethyl ether (DME)

$$2CH_3OH \xrightarrow{-\,H_2O} CH_3OCH_3$$

b.p. -24.8 °C; m.p. -141 °C

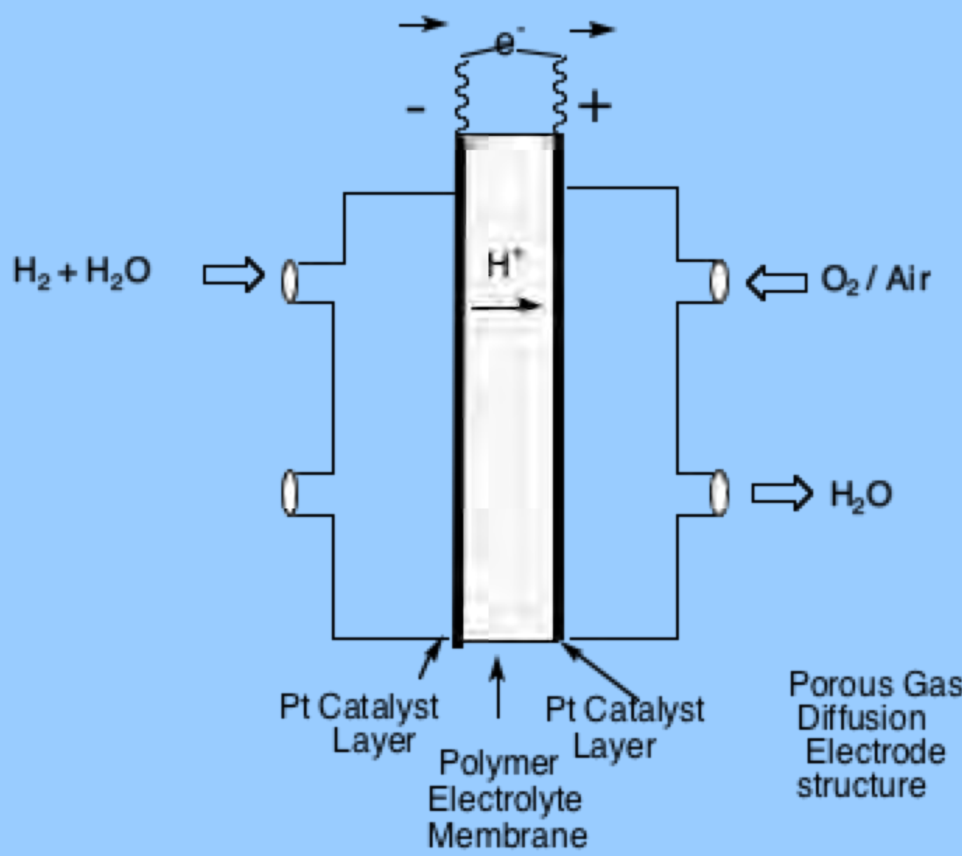
- ❖Excellent diesel fuel substitute with a cetane number of 55-60 (45-55 for regular diesel)
- ❖Very clean burning (extremely low NO_x, SO_x and PM)
- ❖Already used in spray dispenser
- ❖Non-toxic, Safe and does not form peroxides
- ❖Substitute for LNG and LPG
- ❖Easy to produce, ship and dispense
- ❖Sootless flame for glass blowing

DME truck in Japan

DME bus in Denmark

Volvo DME truck in Sweden

Schematic Diagram of a Hydrogen Fuel Cell



Anode	H_2	$\longrightarrow 2H^+ + 2e^-$	$E^0 = 0.00V$
Cathode	$1/2\ O_2 + 2H^+ + 2e^-$	$\longrightarrow H_2O$	$E^0 = 1.23\ V$
Overall	$H_2 + 1/2O_2$	$\longrightarrow H_2O$	$E_{cell} = 1.23\ V$

Advanced methanol-powered fuel cell vehicles

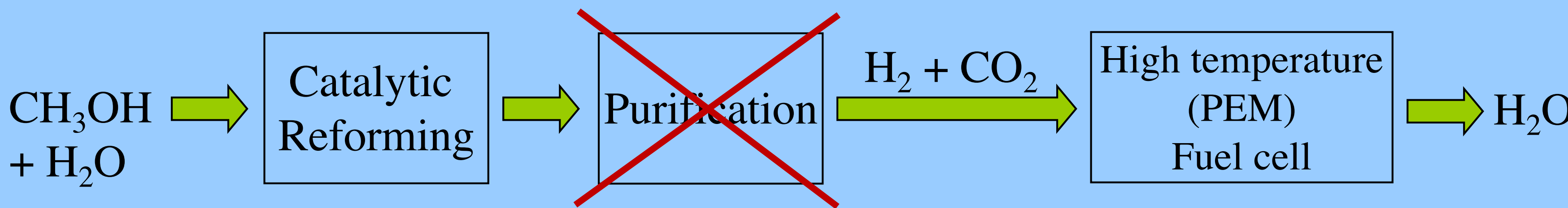
On-board generation of hydrogen through methanol reforming

$CH_3OH + H_2O$ → Catalytic Reforming → Purification → $H_2 + CO_2$ → Proton Exchange membrane (PEM) Fuel cell → H_2O

Methanol has no C-C bonds: reforming at low temperatures (250-300 °C)

Avoids the problem of on-board hydrogen storage under high pressure or in cryogenic liquid form (-253 °C)

Methanol-powered fuel cell as range extender for electric vehicles



High temperature PEM fuel cell more tolerant towards CO poisoning (*Serenergy*, Denmark).

Can be used as a range extender in electrical vehicles and devices.
Hybrid system has lower weight

5 kW HTPEM FC

Range extended from about 150 km to up to 800 km with the HTPEM FC range extender

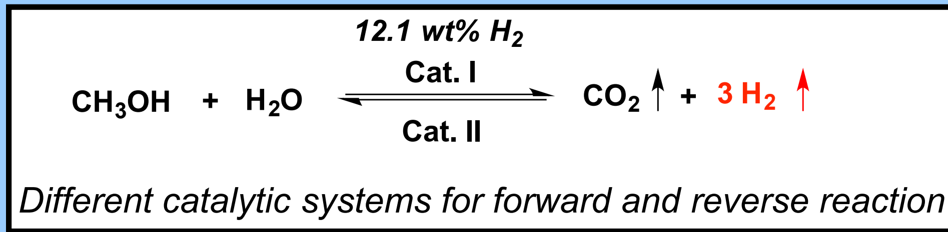
Blue World Technologies, Denmark, 50,000 15 KW stacks

(a) Fiat 5OOe electric car equipped with a Serenergy reformer-PE,MFC range extender fueled by methanol. Source: Courtesy of Serenergy. (b) Methanol fueling station in Denmark besides regular.gasoline and diesel fuel pumps. Source: Courtesy of OK a:m.b.a./ Photo by Ole Hartmann Schmidt. (c) QBEAK III vehicle from ECOmove wjth modular battery and reformer-PEMFC range extender (Serenergy) units. (d) EcoMotion gardening truck powered by Serenergy methanol reformer-PEMFC units. Source: (c,d) Courtesy of EcoMotion with permission

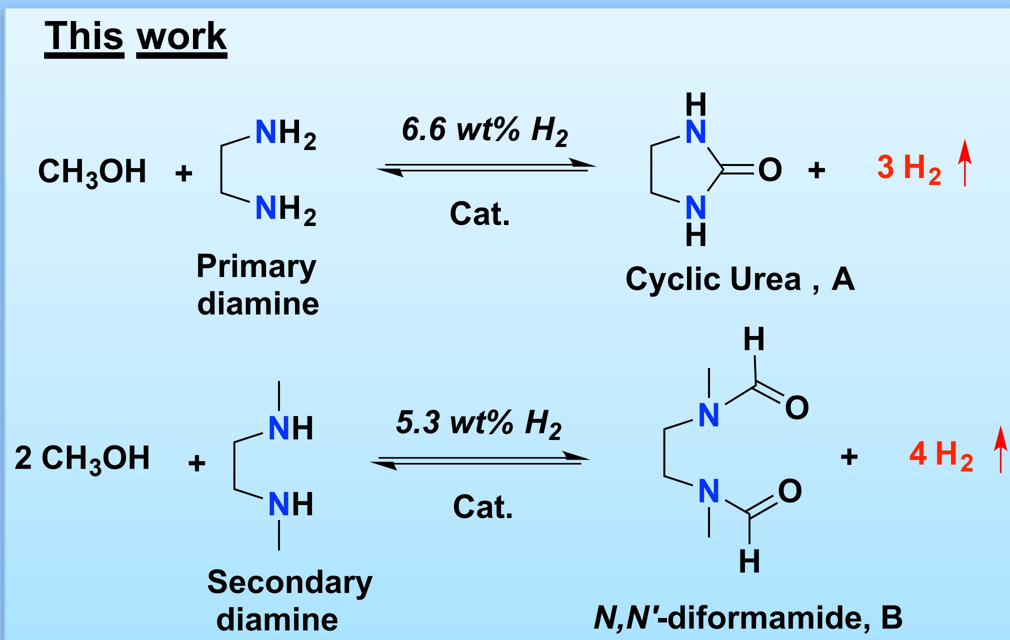
(a) (b)

Palcan hybrid methanol reformer/PEMFC passenger bus (a) and delivery truck (b)

Amine-Promoted Reforming of Methanol



Hydrogenation of CO_2 to methanol and the reverse reaction (2011-to date): Leitner, Sanford, Olah/Prakash, Beller, Hazari, Crabtree, Grutzmacher, Milstein and Fujita.



A CO_2-free hydrogen storage approach

- **Carbon neutral cycle.**
- **Liquid fuel at room temperature.**
- **Clean H_2 gas produced – free of CO_2 and CO.**

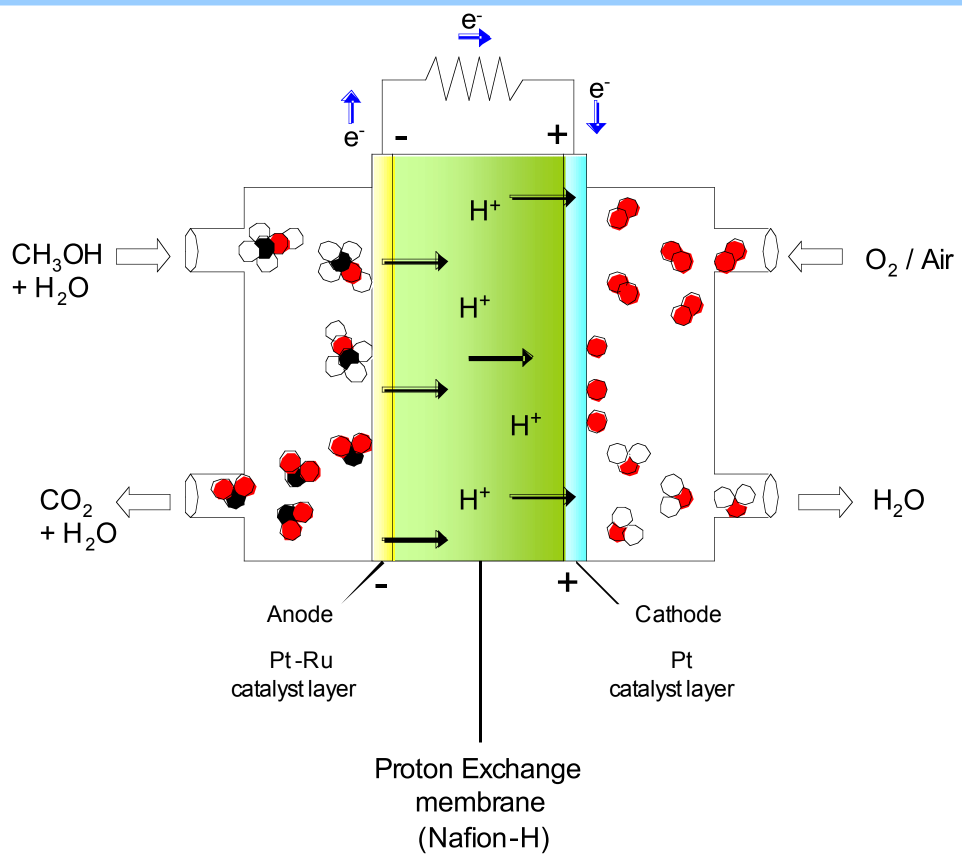
Kothandaraman, J., Kar S., Sen R., Goeppert, A., Olah, G. A. and Prakash, G. K. S. *J. Am. Chem. Soc.* **2017**, 139, 2549-2552.

N-formylation of amines using methanol as a C1 source:

Ortega, N.; Richter, C.; Glorius, F. *Org. Lett.* **2013**, *15*, 1776−1779.

Kim, S. H.; Hong, S. H. *Org. Lett.* **2016**, *18*, 212−215.

Direct oxidation methanol fuel cell (DMFC) USC, JPL - Caltech



Anodic Reaction:

$$CH_3OH + H_2O \xrightarrow{\text{Pt-Ru (50:50)}} CO_2 + 6\,H^+ + 6\,e^-$$

$E^o = 0.006$ V

Cathodic Reaction:

$$3/2\ O_2 + 6\,H^+ + 6\,e^- \xrightarrow{\text{Pt}} 3H_2O$$

$E^o = 1.22$ V

Overall Reaction:

$$CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + H_2O + \text{electricity}$$

$E_{cell} = 1.214$ V

US Patent, 5,599,638, February 4, 1997; ***Eur. Patent*** 0755 576 B1, March 5, 2008.

Direct Methanol Fuel Cell Advantages

❖ **Methanol, 5 kWh/Liter – Theoretical (2 X Hydrogen)**

❖ **Absence of Pollutants**

H_2O and CO_2 are the only byproducts

❖ **Direct reaction of methanol eliminates reforming**

Reduces stack and system complexity

Silent, no moving parts

❖ **Capable of start-up and operation at 20 °C and below**

Thermally silent, good for military applications

❖ **Liquid feed of reactants**

Effective heat removal and thermal management

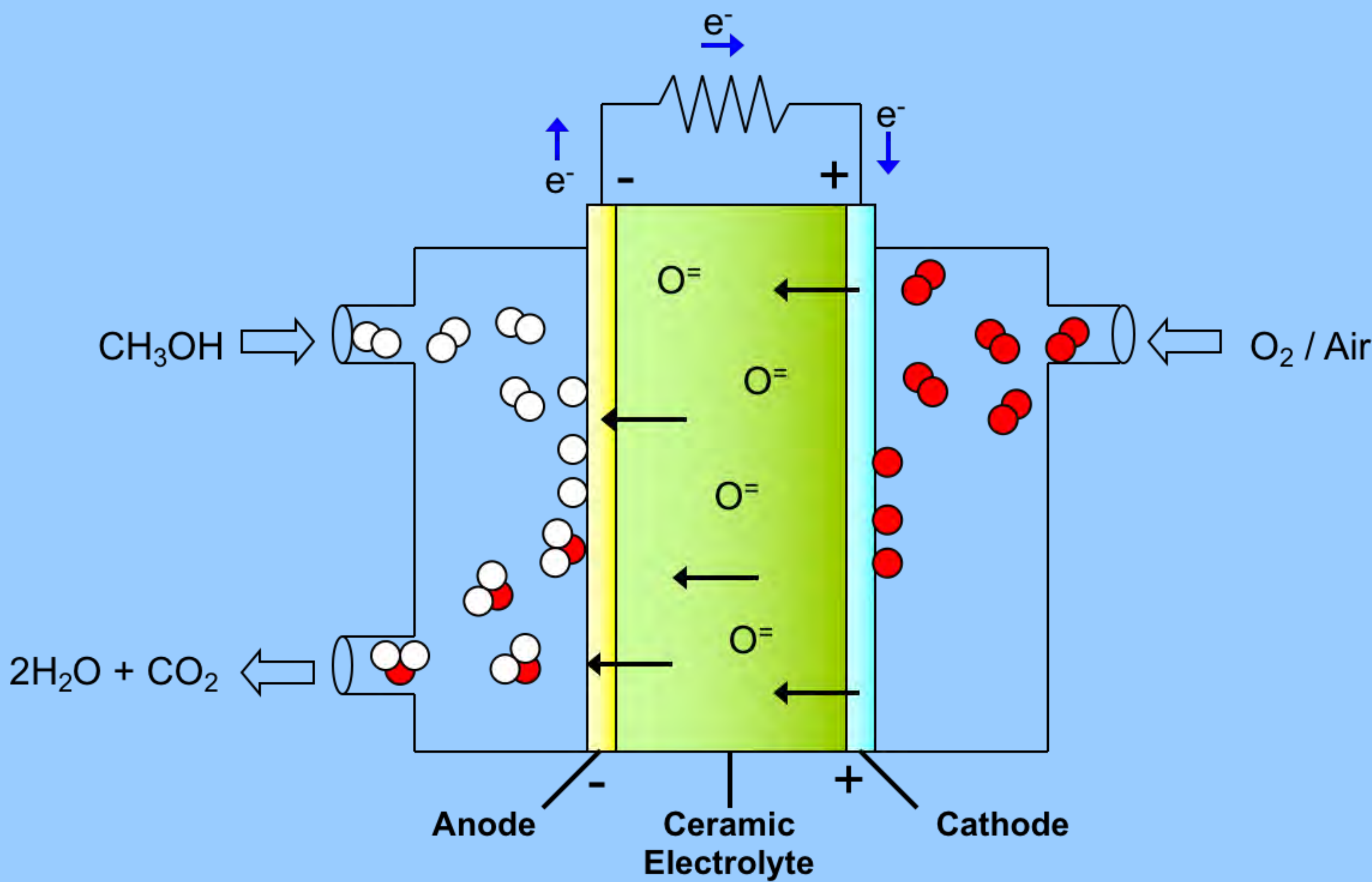
Liquid flow avoids polymer dryout

Convenient fuel storage and logistic fuel

Smart Fuel Cells (SFC), Germany

70 Wh to 3 kWh Portable Devices

Methanol Solid Oxide Fuel Cell (SOFC)



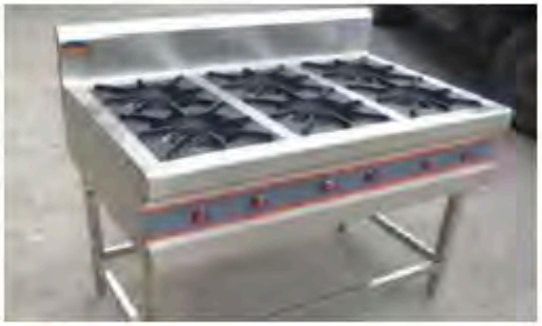
Cathode $3/2O_2 + 6e^- \longrightarrow 3O^=$

Anode $CH_3OH + 3\,O^= \longrightarrow 2H_2O + CO_2 + 6e^-$

Overall $CH_3OH + 3/2O_2 \longrightarrow 2H_2O + CO_2$ + electric energy + heat

Warts ii a 20-kW Methanol SOFC. Source: Courtesy of Wartsila, with permission.

Methanol in Cooking Stove Applications



China is Leading the World

- Methanol for cooking applications in China since 1983
- Available for purchase on Internet
- Current market for 3 million metric tonnes/year, with potential for additional 8 million metric tones of demand
- Use of alcohol in cooking fuels could reduce annual direct coal burning by 3,172 MW and CO_2 emissions decrease of 8.25 billion tons

Methanol CLEANCOOK Stove in Assam, India

Methanol Boiler Fuel

- **Methanol Boiler in Tianjin, 15 steam ton/hour**
- **Currently, 1,000 converted boiler units in China consuming 1 million metric tonnes per year of methanol**

Methanol as a fuel and feedstock

*** Electricity production by combustion in existing gas turbines or boilers**

Interesting for local power generation especially for nations composed of many islands such as Indonesia and the Philippines, where the construction cost of a national grid might be prohibitive.

Eilat , Israel: 50 MW power plant

* **Electricity generation through fuel cells**

Fuel cells not limited by weight and space: other types of fuel cells can be used; PAFC, MCFC and SOFC

***Use of methanol as a cooking fuel in developing countries (Indian Market: 35 Billion litres of methanol)**

Much cleaner burning and efficient than wood or kerosine, ***PROJECT GAIA***

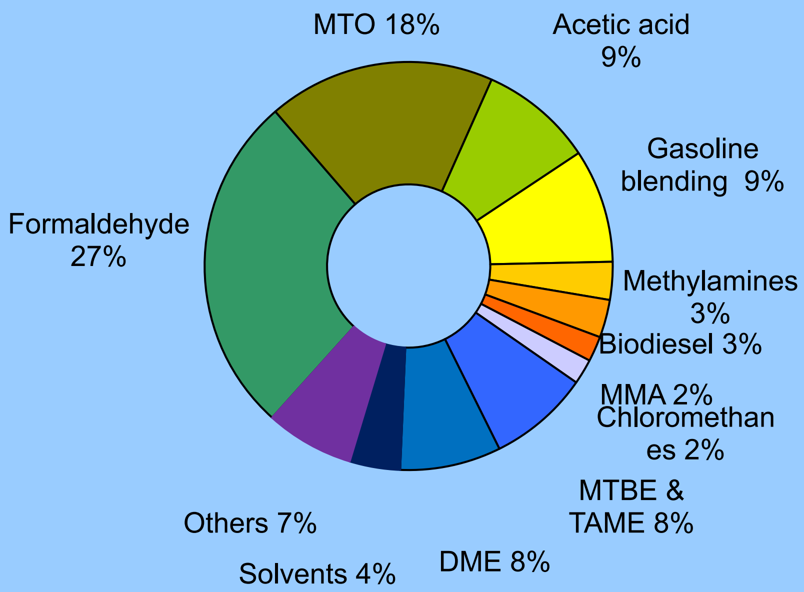
* **Methanol for the production of chemicals**: formaldehyde, MTBE, acetaldehyde, polyethylene, polypropylene and any other chemical obtained from methanol today

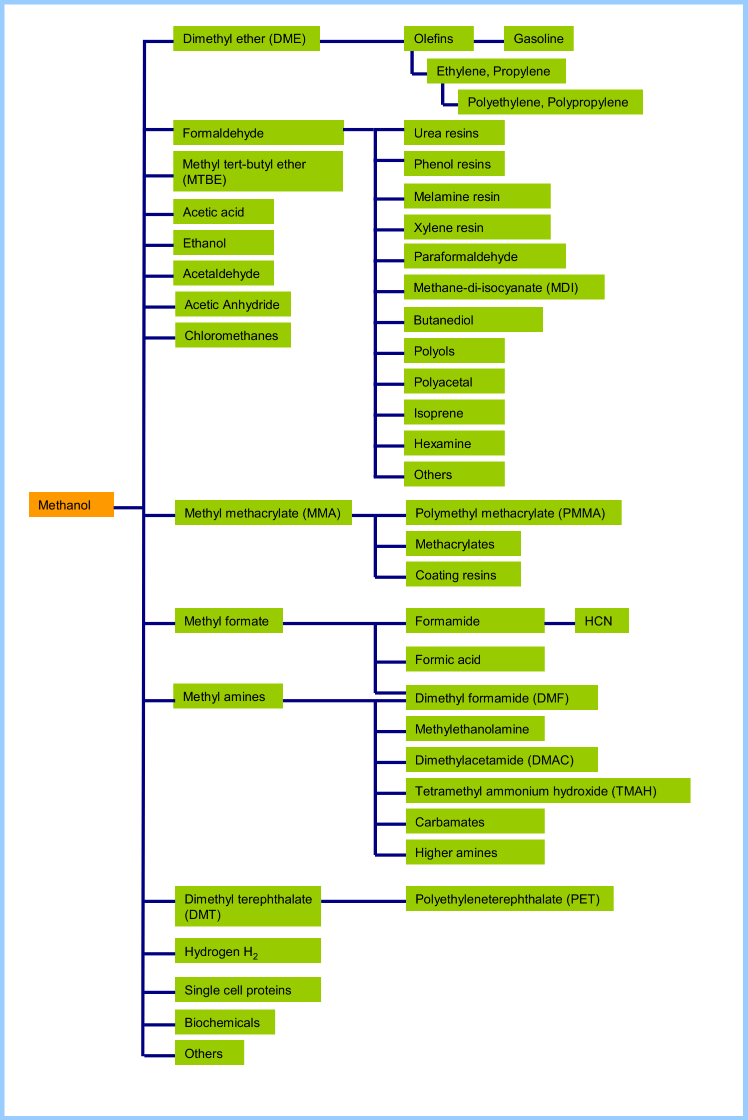
* **Methanol is a feed for single cell proteins-** as a feed for animals

Methanol, a one carbon solution for a one carbon problem

Methanol consumption

Total in 2015: 70 million





Already one of the most important product in the chemical industry

Methanex mega-methanol plant

METHANOL AS HYDROCARBON SOURCE

The MTO (methanol to olefins) Process

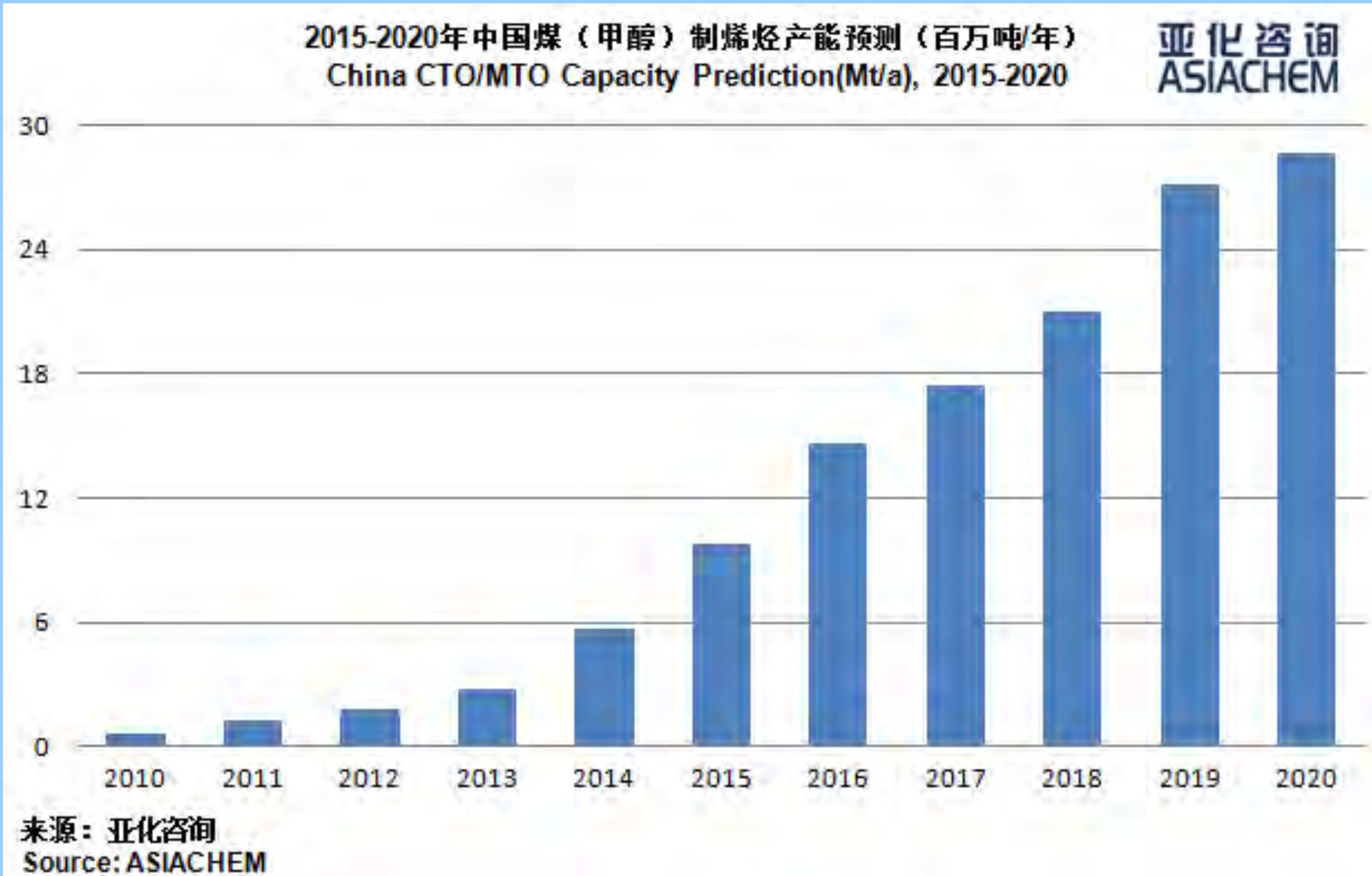
$$2CH_3OH \xrightarrow[\text{Zeolites or bifunctional catalysts}]{-2H_2O} CH_2{=}CH_2\,(CH_3{-}CH{=}CH_2)$$

$$\downarrow$$

HYDROCARBON FUELS AND PRODUCTS

(Gasoline, Diesel, etc.)

All Petrochemical products can be produced from ethylene and propylene including Kerosene (aviation fuel)!


2015-2020年中国煤（甲醇）制烯烃产能预测（百万吨/年）
China CTO/MTO Capacity Prediction(Mt/a), 2015-2020
亚化咨询
ASIACHEM
30
24
18
12
6
0
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
来源：亚化咨询
Source: ASIACHEM

CH_3OH Sources

Industrial Production

Syn-gas (from coal or natural gas)

Direct Methane Conversion

Biomass Gasification

Carbon Dioxide Reduction

Natural Sources

From Wood (wood alcohol)

Recently discovered enormous galactical methanol clouds (460 billion km in diameter near nascent stars)

Future of Natural Gas

An Interdisciplinary MIT Study

2012

FINDING

The potential for natural gas to reduce oil dependence could be increased by conversion into room temperature liquid fuels that can be stored at atmospheric pressure. Of these fuels, methanol is the only one that has been produced for a long period at large industrial scale. Methanol has the lowest cost and lowest GHG emissions, but requires some infrastructure modification and faces substantial acceptance challenges. Natural gas derived gasoline and diesel have the advantage of being drop-in fuels, but carry a higher conversion cost.

CH_3OH from syn-gas

Syn-gas is a mixture of H_2, CO and CO_2

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{298K} = -21.7 \text{ kcal / mol}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{298K} = -11.9 \text{ kcal / mol}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{298K} = -9.8 \text{ kcal / mol}$$

$$S = \frac{\text{moles } H_2}{\text{moles CO}}$$

S=2 ideal for methanol

Syn-gas can be produced from any source of carbon: natural gas, petroleum, coal, biomass, etc.

However, not all give an ideal S ratio for methanol synthesis

CH_3OH from Methane

❖ **Syn-gas from natural gas – steam reforming (SMR)**

$$CH_4 + H_2O \xrightleftharpoons{\text{Ni Cat.}} CO + 3H_2 \qquad \Delta H_{298K} = 49.1 \text{ kcal / mol}$$

S=3

Excess H_2 generally used for ammonia (NH_3) production

❖ **Partial oxidation of methane**

$$CH_4 + 1/2\ O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H_{298K} = -8.6 \text{ kcal / mol}$$

$$CO + 1/2\ O_2 \rightleftharpoons CO_2 \qquad \Delta H_{298K} = -67.6 \text{ kcal / mol}$$

$$H_2 + 1/2\ O_2 \rightleftharpoons H_2O \qquad \Delta H_{298K} = -57.7 \text{ kcal / mol}$$

S=2

❖ **Dry reforming with CO_2 (DMR)**

$$CO_2 + CH_4 \xrightleftharpoons{\text{Ni Cat.}} 2CO + 2H_2 \qquad \Delta H_{298K} = 59.1 \text{ kcal / mol}$$

S=1

Reactions occur at high temperatures (at least 800-1000 °C)

Combination of Steam Reforming and Partial oxidation of Methane:
Autothermal Reforming

Bireforming of Methane

Steam Reforming $2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2 \quad \Delta H_{298K} = 98.4$ kcal / mol

Dry Reforming $CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad \Delta H_{298K} = 59.1$ kcal / mol

Bireforming $3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2 \quad \Delta H_{298K} = 157.5$ kcal / mol

Metgas

$\downarrow$

$4CH_3OH$

The production of methanol is generally conducted at pressures of 30 to 100 bars. Conducting the steam and dry reforming or the bireforming at higher pressure would therefore be also advantageous to avoid the need for compression of the syn-gas.

Bireforming allows the use of natural gas resources containing CO_2 without need for separation.

***US Patent*, 7,909,559, March 15, 2011**
***US Patent*, 8,133,926, March 13, 2012**
***US Patent*, 8,440,729, March 14, 2013**

G. A. Olah, A. Goeppert, M. Czaun, T. Mathew, R. B. May and G. K.S. Prakash, *J. Am. Chem. Soc*. **2015**, 137, 8720-8729.

Oxidative Bi-reforming and Methanol Synthesis

Methane combustion

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H_{298K} = -191.9 \text{ kcal/mol}$$

After admixing fresh methane, bi-reforming is carried out

$$3CH_4 + 2H_2O + CO_2 \longrightarrow \underbrace{4CO + 8H_2}_{\text{metgas}} \qquad \Delta H_{298K} = 157.5 \text{ kcal/mol}$$

Methanol synthesis

$$4CO + 8H_2 \longrightarrow 4CH_3OH \qquad \Delta H_{298K} = -86.8 \text{ kcal/mol}$$

Overall reaction

$$4CH_4 + 2\,O_2 \longrightarrow 4CH_3OH \qquad \Delta H_{298K} = -121.2 \text{ kcal/mol}$$

G. A. Olah, G. K. S. Prakash, A. Goeppert, M. Czaun, T. Mathew, *J. Am. Chem. Soc,* **2013**, *135*, 10030-10031; G. A. Olah, A. Goeppert, M. Czaun, T. Mathew, R. B. May and G. K.S. Prakash, *J. Am. Chem. Soc*. **2015**, 137, 8720-8729;. ***US Patent*, 8,697,759, April 15, 2014.**

CH_3OH from coal
A proven technology

$$3C + 3/2\, O_2 \xrightarrow{\text{Catalysts}} 3CO$$

$$2CO + 2H_2O \longrightarrow 2CO_2 + 2H_2$$

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$3C + 2H_2O + 3/2\, O_2 \longrightarrow 2CO_2 + CH_3OH$$

$$C + H_2O \rightarrow CO + H_2$$

China is currently adopting this approach on a massive scale based on its large coal reserves

100 plants in construction or planned!

A combination of steam and oxygen is used in coal reforming

Due to the low H/C ratio of coal: a lot of CO_2 is produced!

Methanol from biomass

•Biomass includes any type of plant or animal material:
Wood, wood wastes, agricultural crops and by-products, municipal waste, animal waste, aquatic plants and algae, etc.

•Transformed to methanol by gasification through syngas- very efficient

Biomass ⟶ Syn-gas ($CO + H_2$) ⟶ Methanol

•Any biomass is fine to make methanol

•Large amount of biomass needed- can convert biomass to biocrude and it can be shipped.

Biocrude

•Methanol from Biogas (mixture of CH_4, CO_2)

•Methanol through aquatic biomass- micro-algae

Biomass alone can not fulfill all our increasing energy needs

Biomass to Liquids (Methanol)

Lignocellulose

↓ Fast Pyrolysis, 550 °C

Condensate + Char + Slurry, 90%

↓ Gasification with Oxygen, 1200 °C

$CO + H_2$ Syngas, 78%

↓

Methanol or other liquids

Bio-DME from Black Liquor

Paper manufacturing

↓

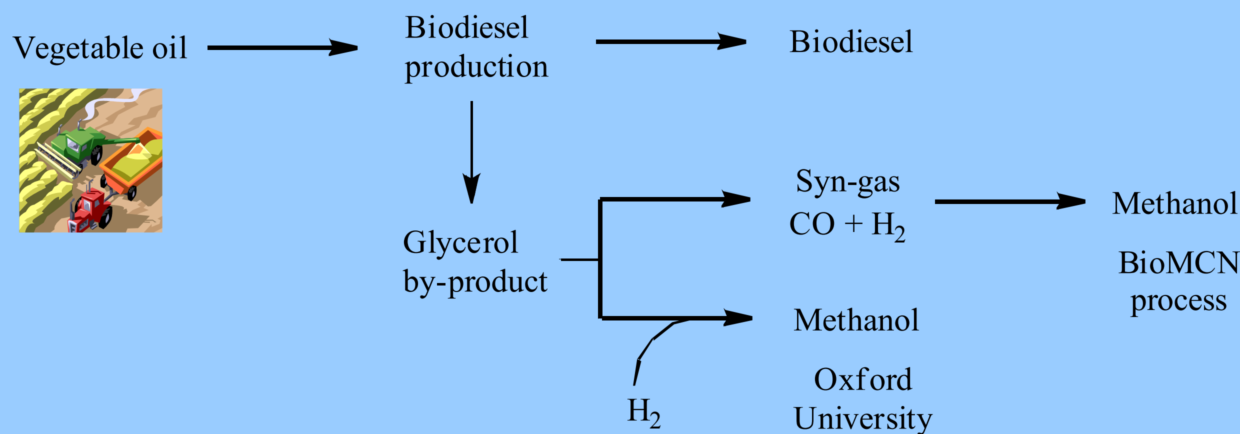
Black liquor by-product → Syn-gas $CO + H_2$ → DME

CHEMREC pilot plant in Sweden (4 t/day Bio-DME)

Bio-DME filling station

Volvo DME powered truck

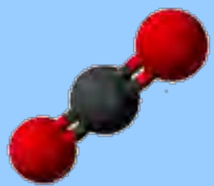
Bio-Methanol from Glycerol

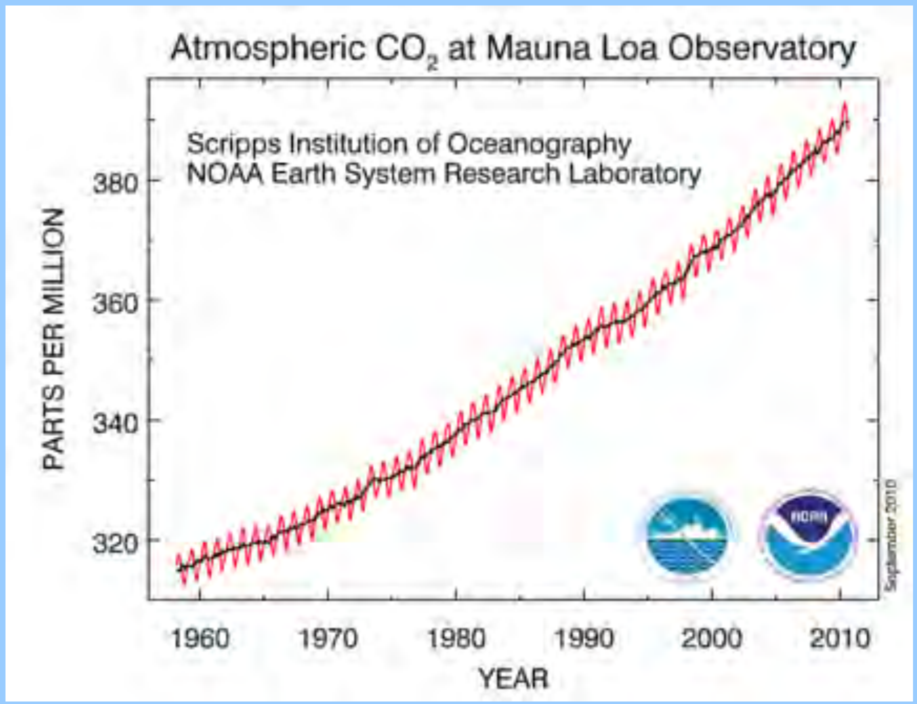


BioMCN commercial methanol plant
with a 200 000 kT/year capacity
The Netherlands

Further expansions in steps of 200 000 kT capacity planned

Why Focus on Carbon Dioxide?





- Linear molecule
- Very stable
  - Difficult to efficiently reduce
- Trace gas
  - 0.040% of the atmosphere
  - Amount of CO_2 in the atmosphere is increasing
- With declining fossil fuel reserves, CO_2 will become the best source of carbon

US Patent, 7,605, 293, October, 20, 2009
US Patent, 7,608, 743, October, 27, 2009

Sources of CO_2

Geothermal Vents
Fermentation Processes
Natural Gas Wells
Cement Plants

Fossil Fuel Burning Power Plants
Aluminum Plants
Air Itself

CO_2 separation and Capture technologies

- Absorption
  - Chemical
    - MEA, DEA
    - KOH, NaOH, MgO
    - Etc.
  - Physical
    - Solexol
    - Rectisol
    - Etc.
- Adsorption
  - Alumina
  - Zeolite
  - Activated carbon
- Cryogenics
  - Dry ice formation at low temperature
- Membranes
  - Polymer based
    - Poly(phenylene oxide)
    - Poly(ethylene oxide)
    - Poly(ionic liquid)
  - Inorganic membranes
    - Ceramic based
    - Zeolite based
- Algal and microbial systems

Regeneration method (Absorption, Adsorption)
- Pressure swing
- Temperature swing
- Moisture swing
- And combination thereof

Efficient capture from air remains challenging

Why capture CO_2 from the air?

Important to address ~ 50% of anthropogenic CO_2 emissions from small distributed sources such as home and office heating and cooling and the transportation sector

Collection of CO_2 from billions of small fossil fuel burning units at the source is difficult and not practical and/or economical

Direct air capture (DAC) of CO_2 would allow the collection of CO_2 from any source, small or large, static or mobile.

Independence from CO_2 point source means the capture unit could be placed anywhere, offering considerable flexibility

Lower concentration of contaminants such as NO_x, SO_x and particulates in air compared to flue gases

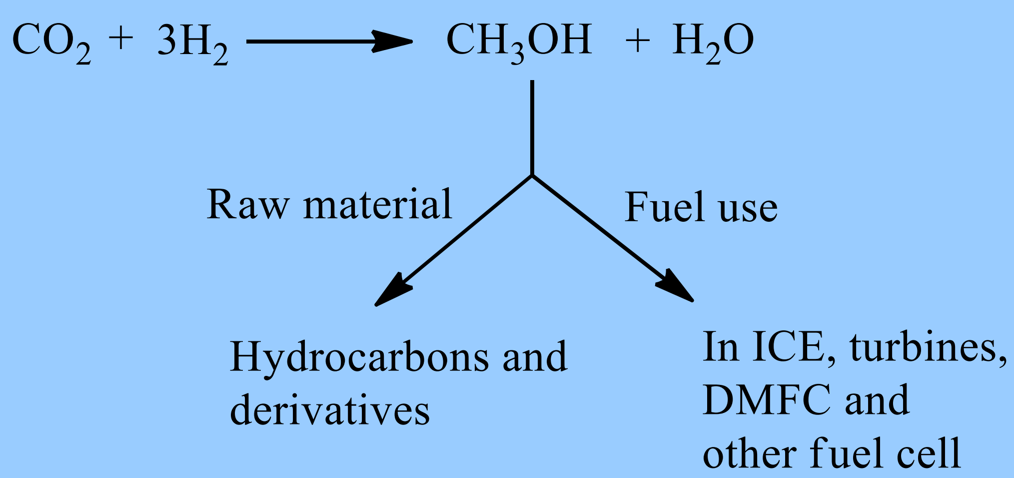
Eventually, DAC could even be used to lower atmospheric CO_2 concentrations

Work on CO_2 capture from the air at the Loker Hydrocarbon Research Institute

We decided to focus our effort on finding an easy to prepare, inexpensive but at the same time efficient adsorbent based on a Class 1 hybrid material : fumed silica based materials

Interest for various reasons:

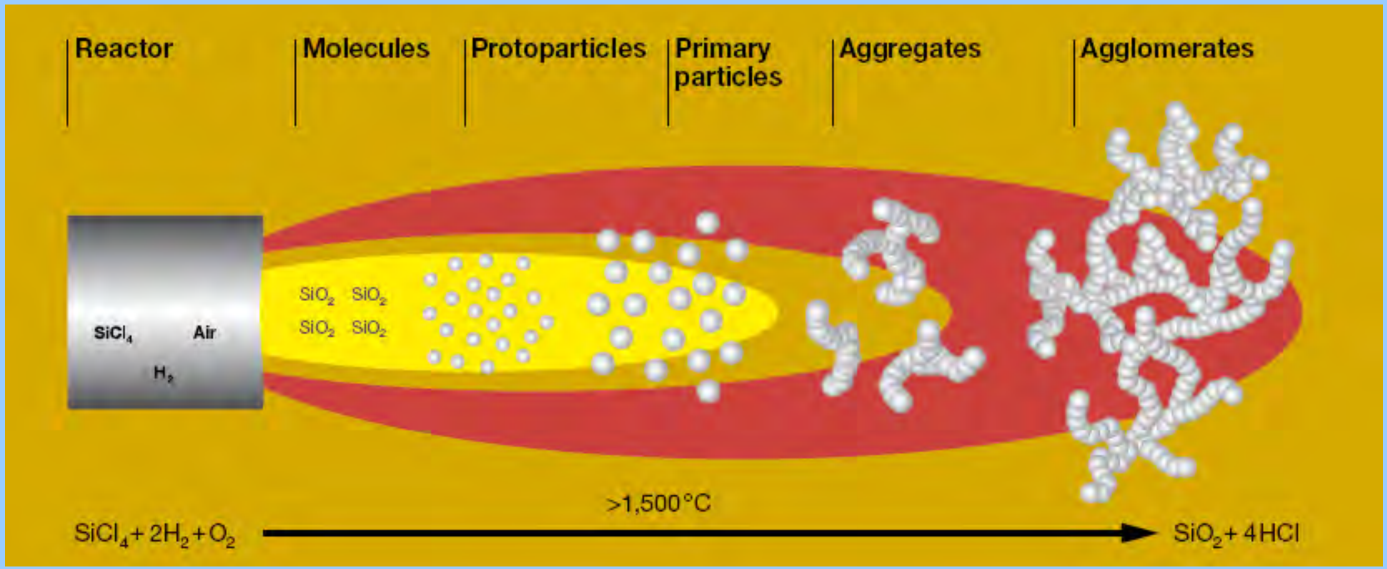
- Capture of CO_2 for recycling to fuels and materials such as methanol, DME, hydrocarbons (methanol economy)



- Capture of CO_2 to produce CO_2 free air for use in iron/air batteries with an alkaline electrolyte (ARPA-e)

-Indoor air quality (reduce the amount of CO_2 in enclosed spaces)

Support characteristics
Fumed silica synthesis



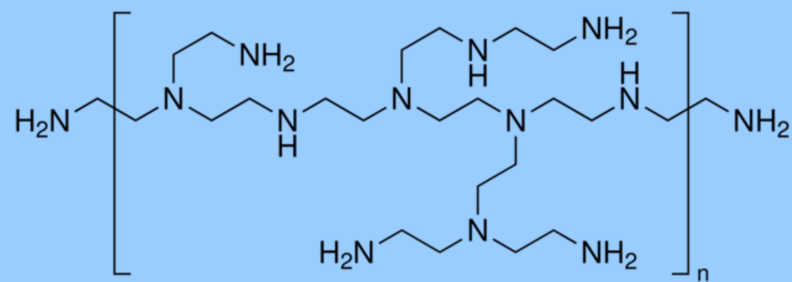
Fumed silica: primary particle size ~ 7 nm, fluffy powder, very low density

Absorbent support	Pore volume (cm^3/g)	Bulk tapped density (cm^3/g)	Volume between particles (cm^3/g)
Fumed SiO_2 (Aldrich)	0.961	~ 20	~ 19
Fumed SiO_2 (Aerosil 300)	0.714	~ 20	~ 19
Fumed SiO_2 (Aerosil 150)	0.426	~ 20	~ 19
Precipitated SiO_2 (Hi-Sil T-600)	0.704	~ 20	~ 19
Silica gel	1.094	2.55	~ 1

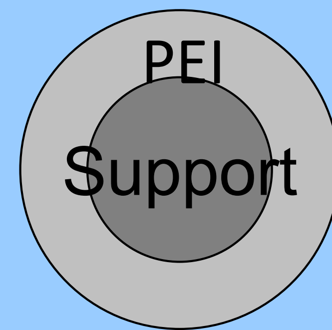
Presence of large volume mesopores and macropores to which PEI can easily access and still allow facile CO_2 diffusion

Solid hybrid adsorbent preparation

Structure of branched polyethylenimine (PEI)



PEI (HMW)
Mw ca. 25000



Solid support: fumed silica (300-380 m^2/g)

Prepared easily by

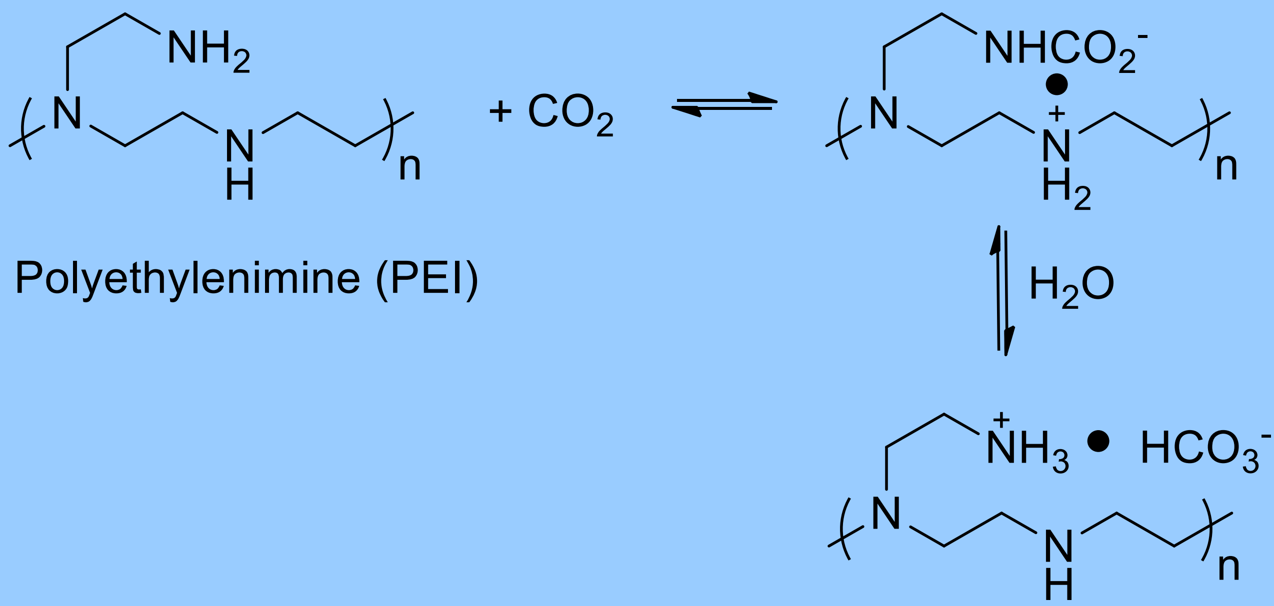
- Dissolving the polyamine in methanol and mixing the solution into a suspension of support in methanol.
- Evaporation of the solvent and drying.

Adsorbent	PEI content
FS-PEI-50	50%
FS-PEI-33	33%
FS-PEI-25	25%
FS-PEI-20	20%

Can be prepared in a very short period of time

Goeppert, A.; Meth, S.; Prakash, G. K. S.; Olah, G. A. *Energy Environ. Sci.* **2010**, *3*, 1949

Reaction of polyethylenimine (PEI) with CO_2



Polyethylenimine (PEI)

Carbamate

½ CO_2 per amine

Bicarbonate

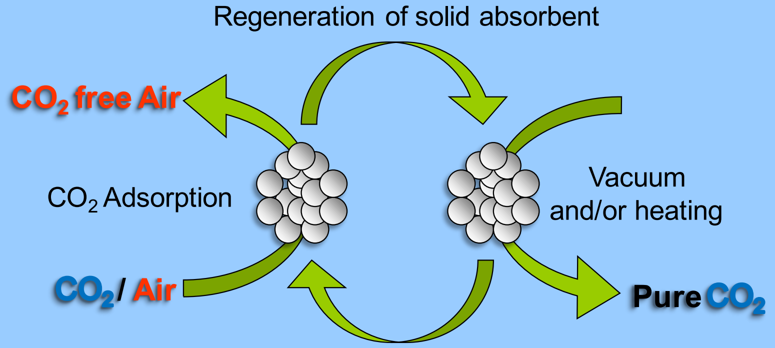
1 CO_2 per amine

Under dry conditions: carbamate formation. Two amino groups needed for each CO_2 molecule

Under humid conditions: bicarbonate formation. In theory only one amino group needed for each molecule of CO_2

Desorption techniques for organic-based adsorbents

Temperature swing adsorption (TSA)
Adsorption at RT
Desorption at higher temperature (70-200 °C) with or without a swiping gas

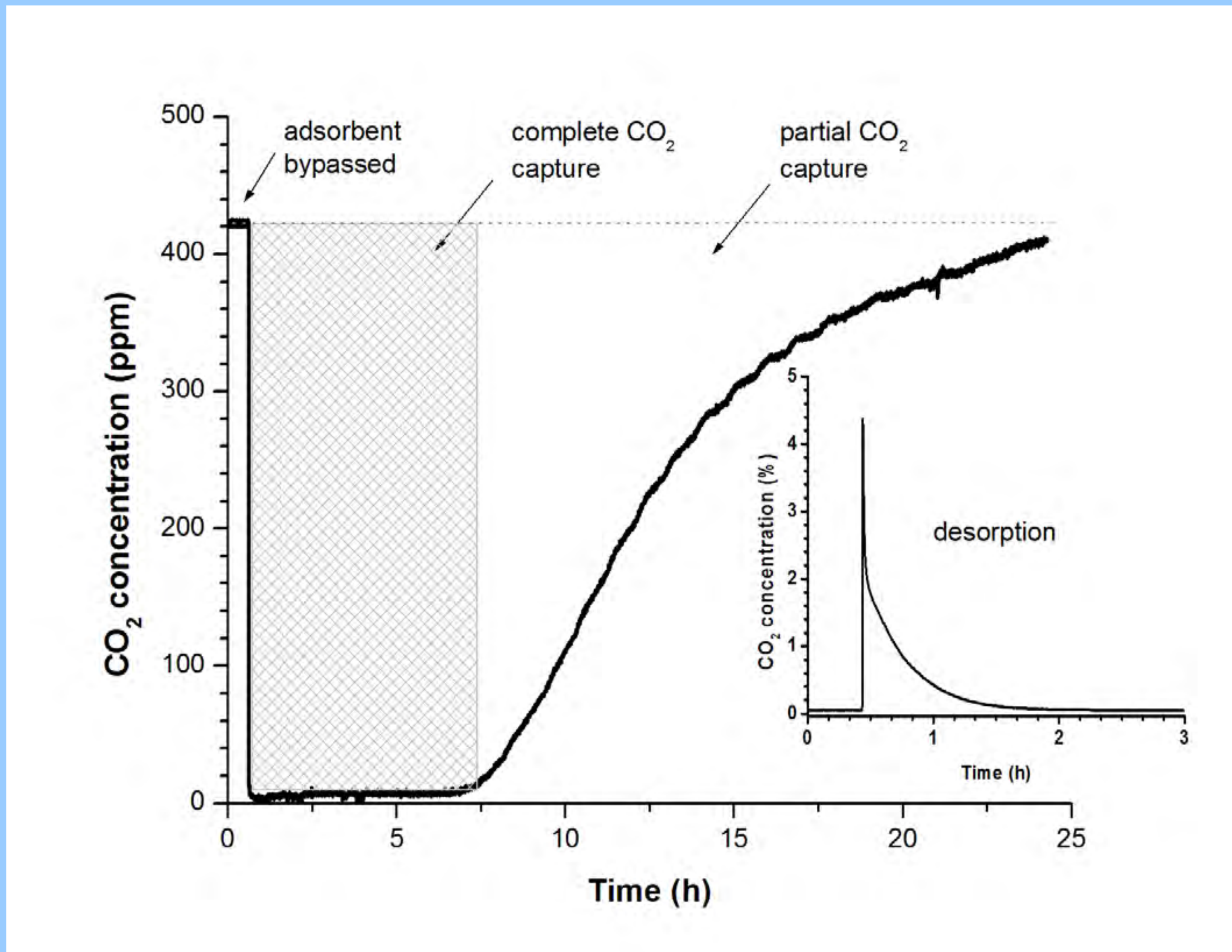


Vacuum swing adsorption (VSA)
Adsorption at atmospheric pressure
Desorption under vacuum

Electrical thermal swing adsorption (ETSA)
Electrical current applied to the electrically conducting sorbent (e.g. carbon) to release CO_2

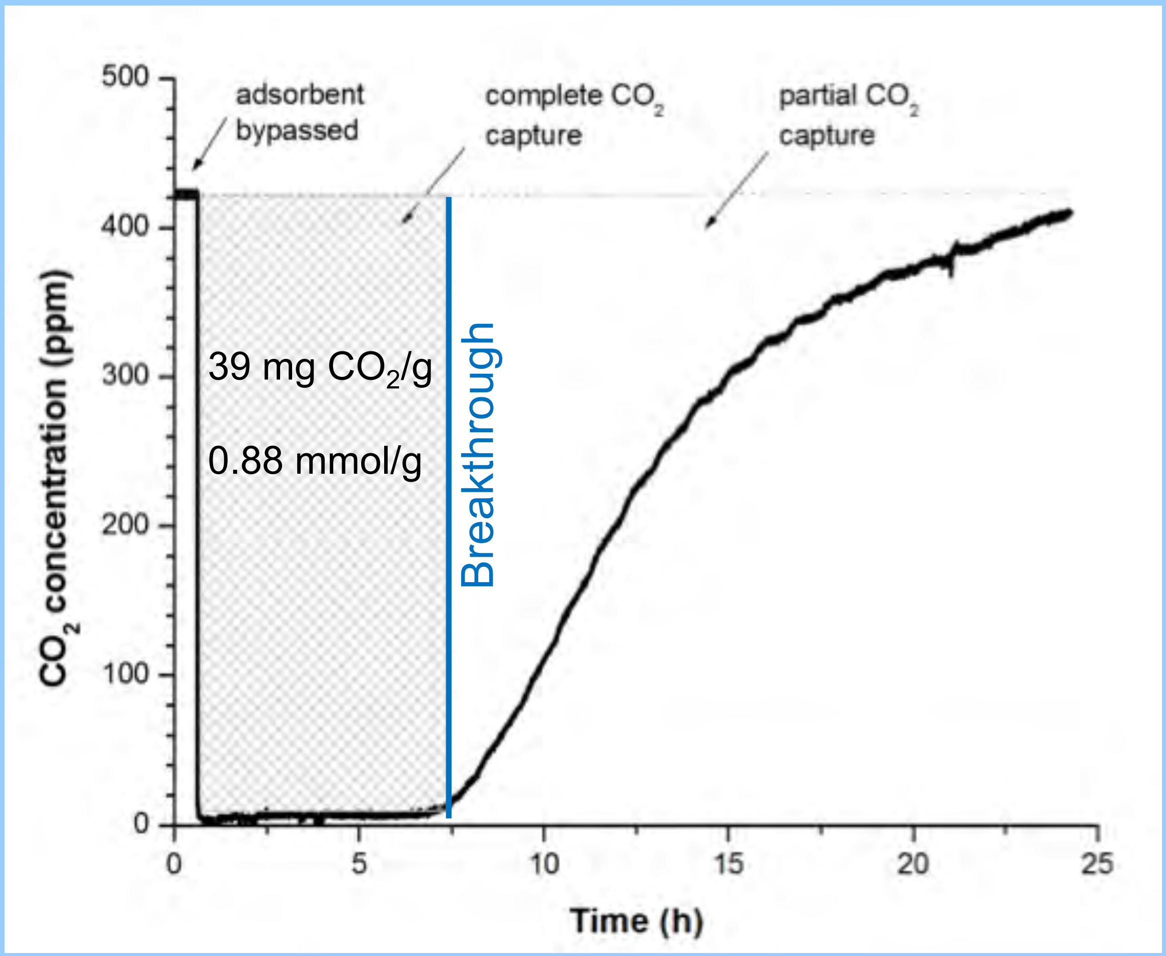
Combination of techniques
VSA with TSA: TVSA

Adsorption of CO_2 from the air at 25 °C on PEI/Fumed Silica
Inset: Desorption at 85 °C

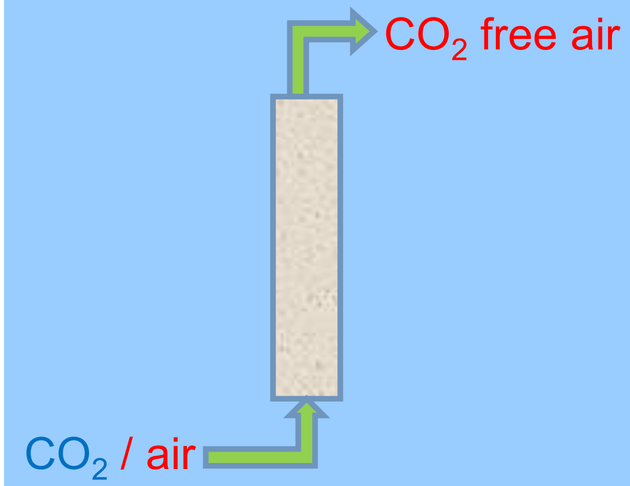


Goeppert, A.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R. *J. Am. Chem. Soc*. **2011**, *133*, 20164

Adsorption of CO_2 from the air at 25 °C on FS-PEI-50 (PEI/fumed silica 1/1)



Total CO_2 adsorption:
75 mg/g
1.71 mmol/g

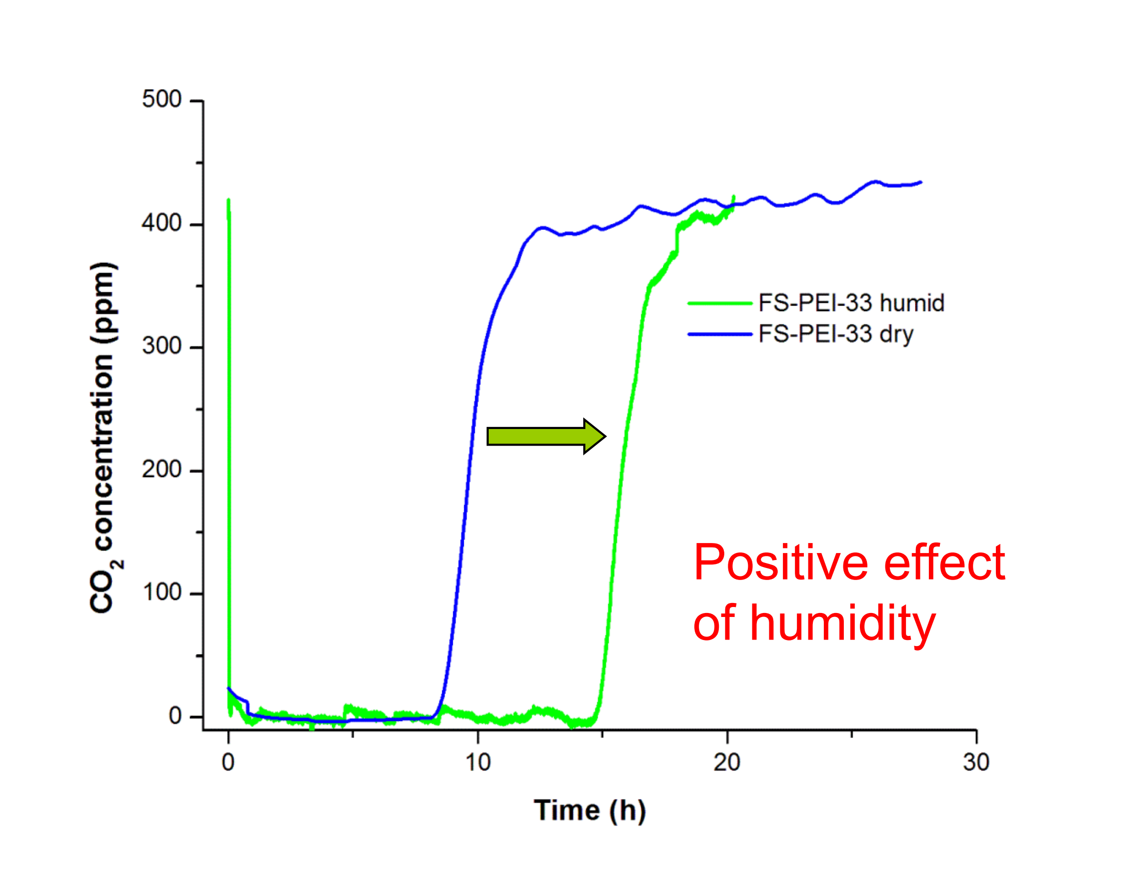


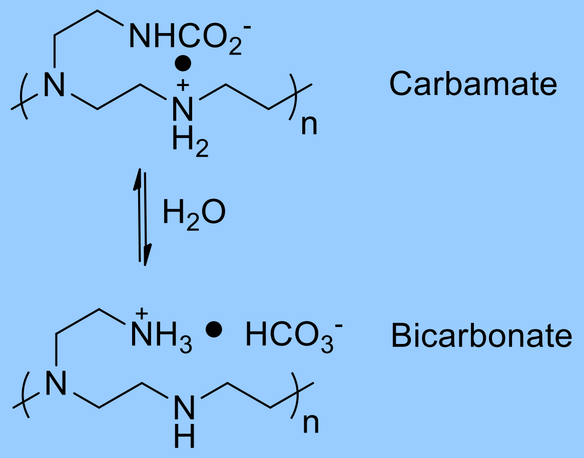
Amount of catalyst : 2.72 g
Flow rate: 335 mL/min air

Goeppert, A.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R. *J. Am. Chem. Soc*. 2011, *133*, 20164

Adsorption of CO_2 from the air at 25 °C on FS-PEI-33. Effect of humidity

Conditions	mg/g adsorbent	mmol/g adsorbent	mg/g PEI	mmol/g PEI
Dry	52	1.18	156	3.55
Humid	78	1.77	234	5.32



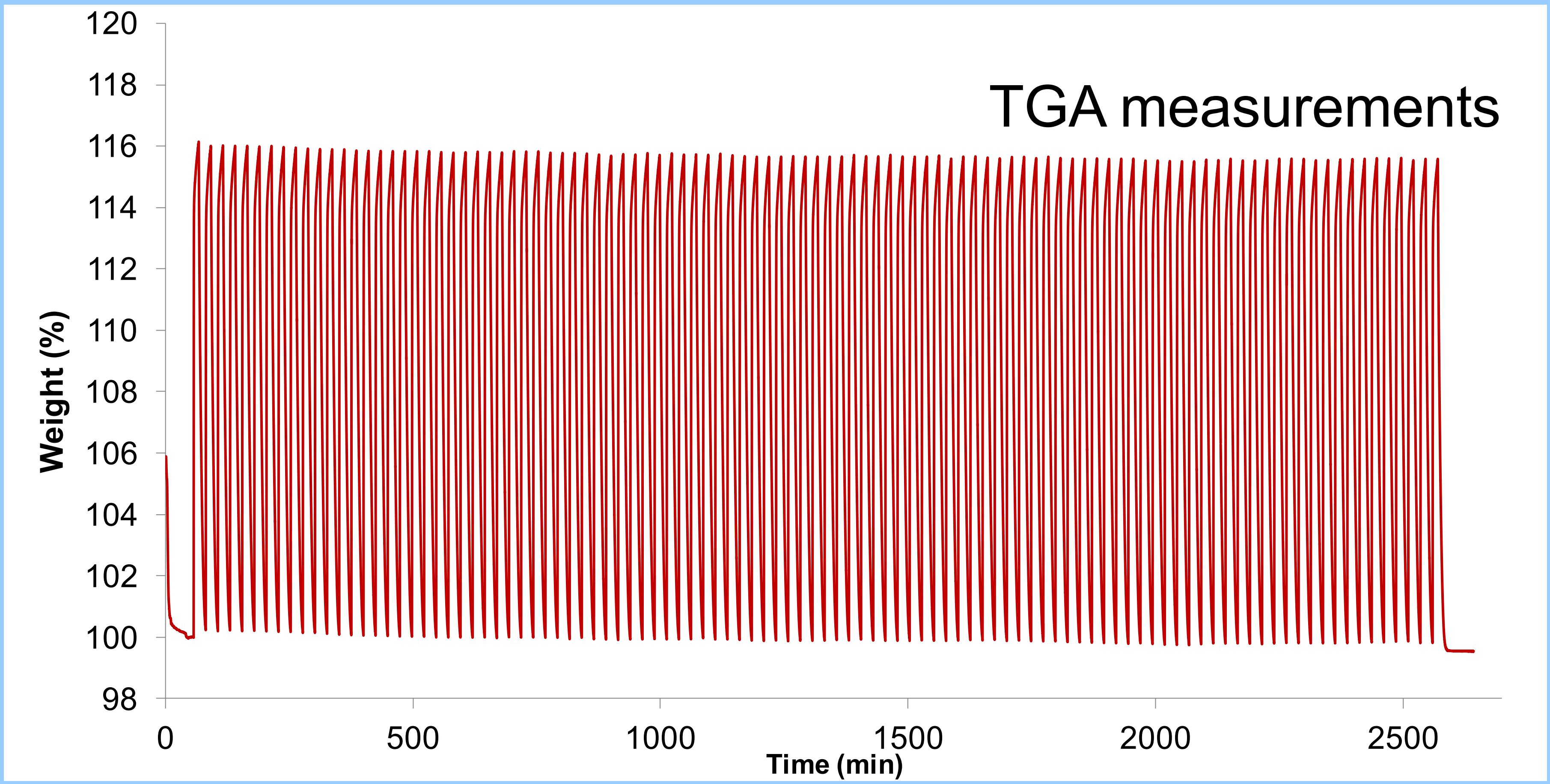


Consistent with the formation of bicarbonates

Humid conditions: 67% relative humidity at 25 °C

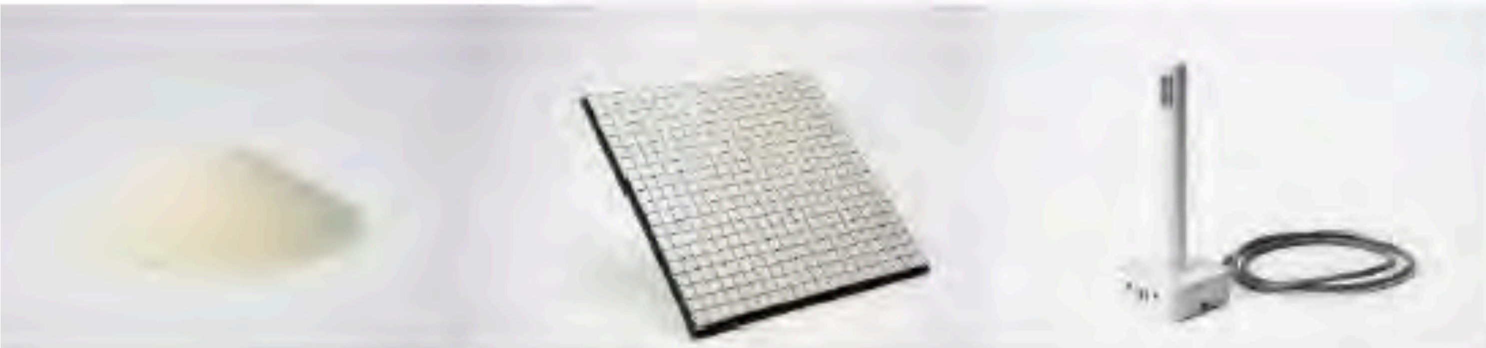
In the case of zeolites, humidity stops the adsorption of CO_2 almost entirely

Example of CO_2 adsorption/desorption (100 cycles)



No significant loss in adsorption capacity under CO_2/N_2
(157 mg CO_2/ g adsorbent)

Deep technology and expertise around materials, systems and air management.



1
Blend of novel, hybrid sorbents captures a wide range of contaminant molecules

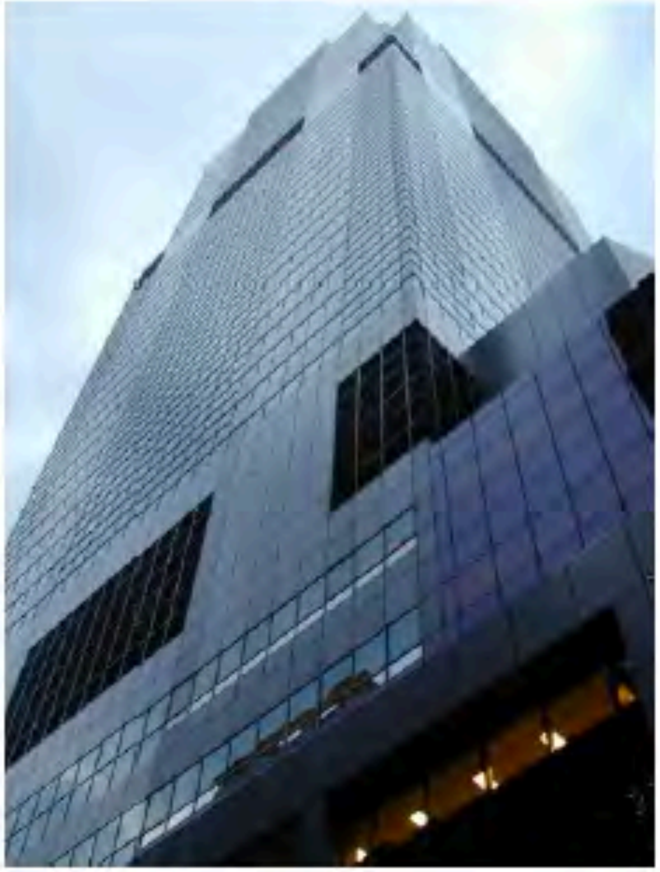
2
Sorbent blend is arranged in proprietary, replaceable cartridges

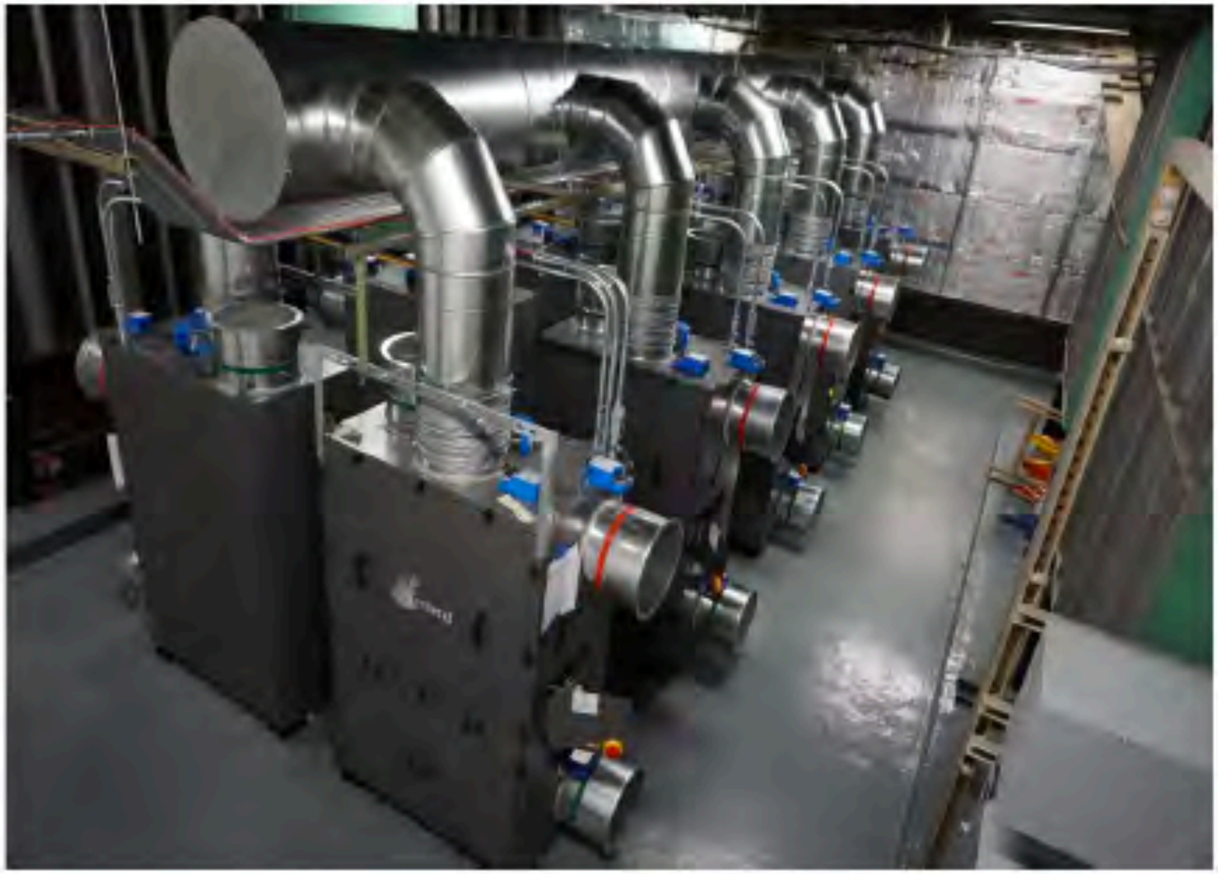
3
Specialized sensors track and monitor air quality

4
Electronics + software control and optimize performance

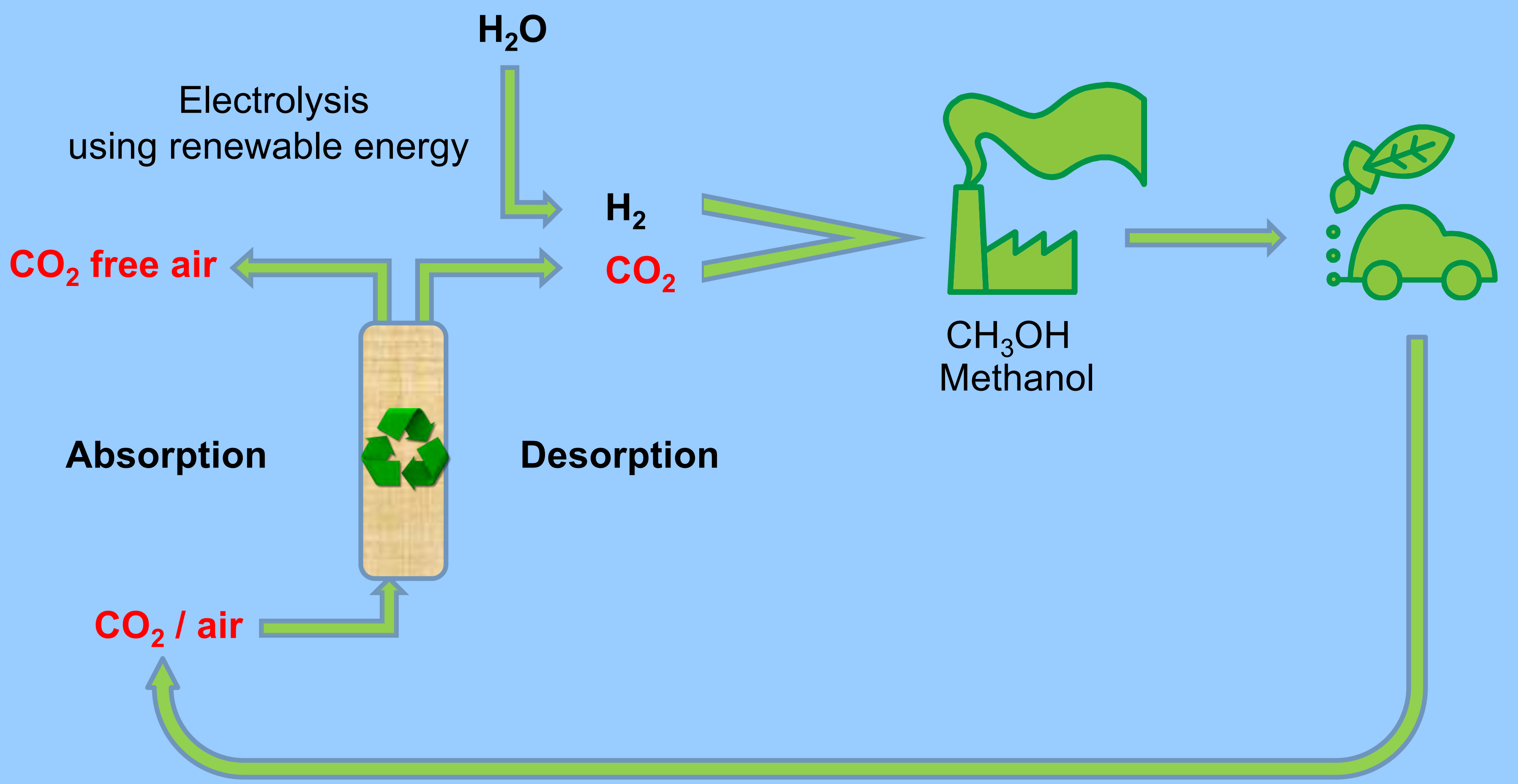
70+ patents

Scalable solution for any size building

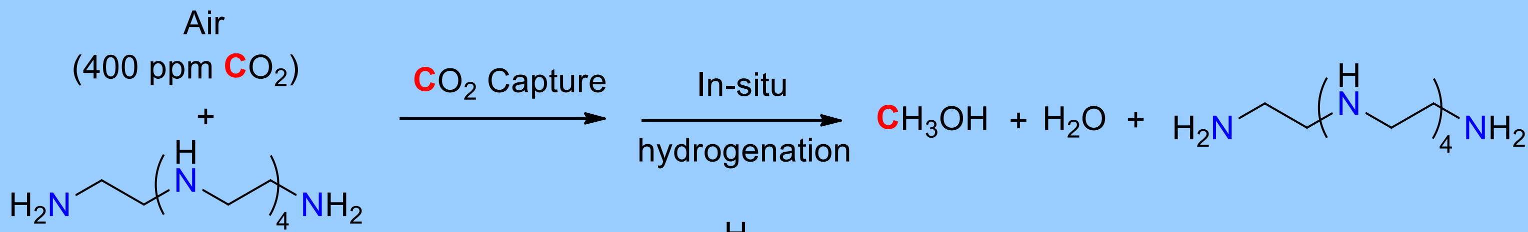


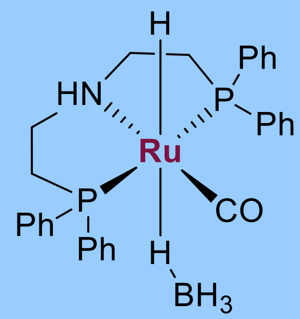


Capture of CO_2 from the Air and Recycling to Fuels and Materials



Capture of CO_2 from the air and recycling to methanol under homogeneous conditions





1

CO_2 capture from air and conversion to CH_3OH

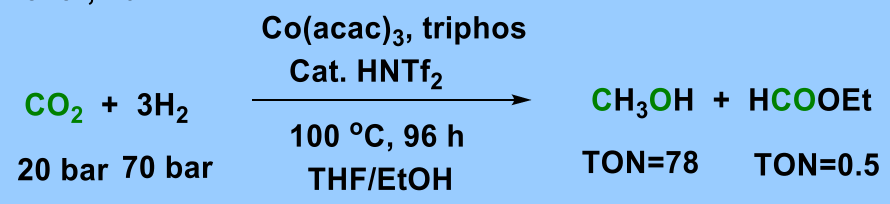
Entry	Amine	CO_2 captured (mmol)	Solvent	CH_3OH (mmol)	NMR Yield (%)
1	PEHA	5.4	1,4-Dioxane	2.1	39
2	PEHA	5.4	Triglyme	3.3	61
3[a]	PEHA	5.4	Triglyme	4.3	79

Reaction condition: PEHA=3.4 mmol, catalyst **1**=20 μmol, H_2=50 bar, t=40h, T=155 °C and organic solvent (10 mL)-H_2O (8 mL). [a]t=55h.

J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, J. Am. Chem. Soc., **2016**, *138*, 771-778.

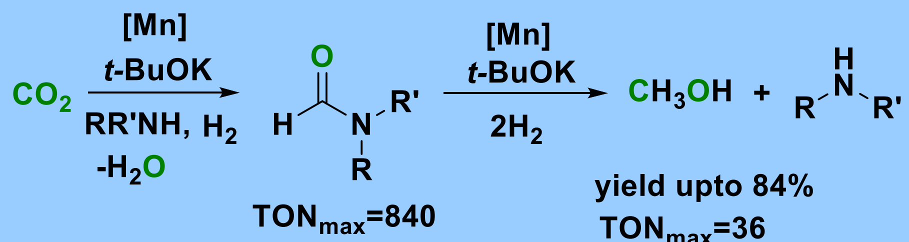
Manganese-Catalyzed Hydrogenation of CO_2 to Methanol

Beller, 2017

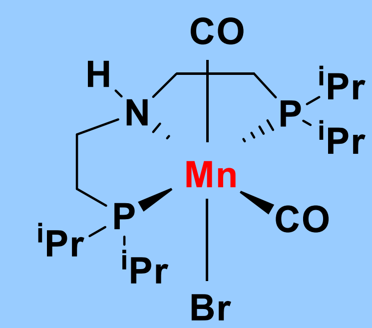


Schneidewind, J.; Adam, R.; Baumann, W.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 1890–1893.

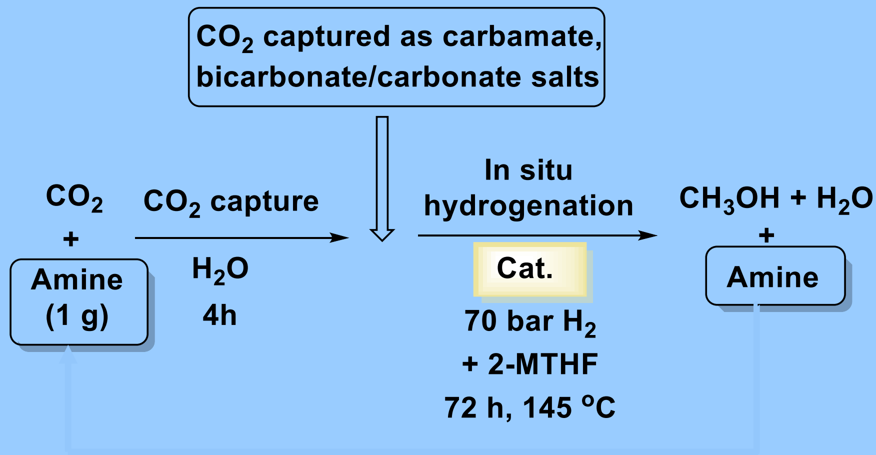
Prakash, 2017

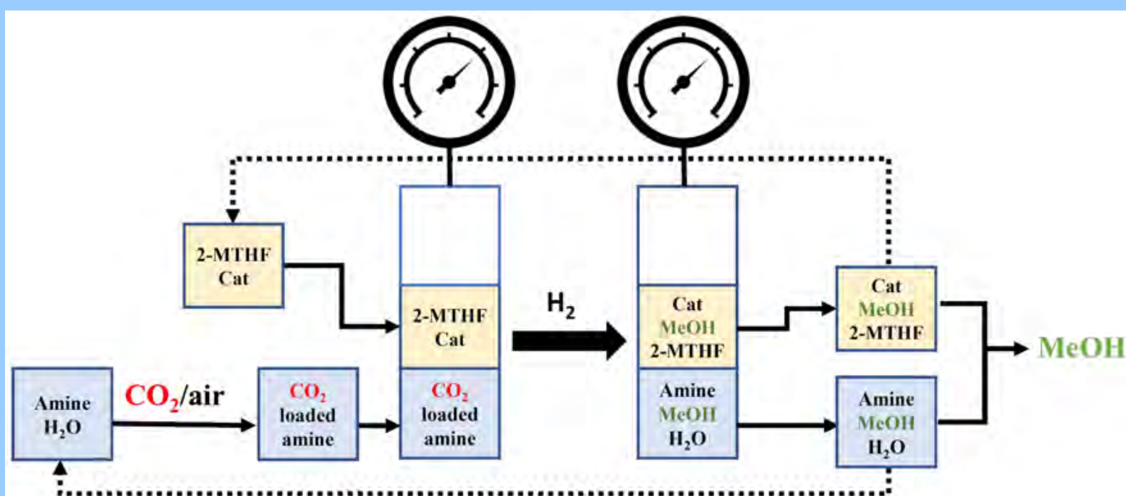


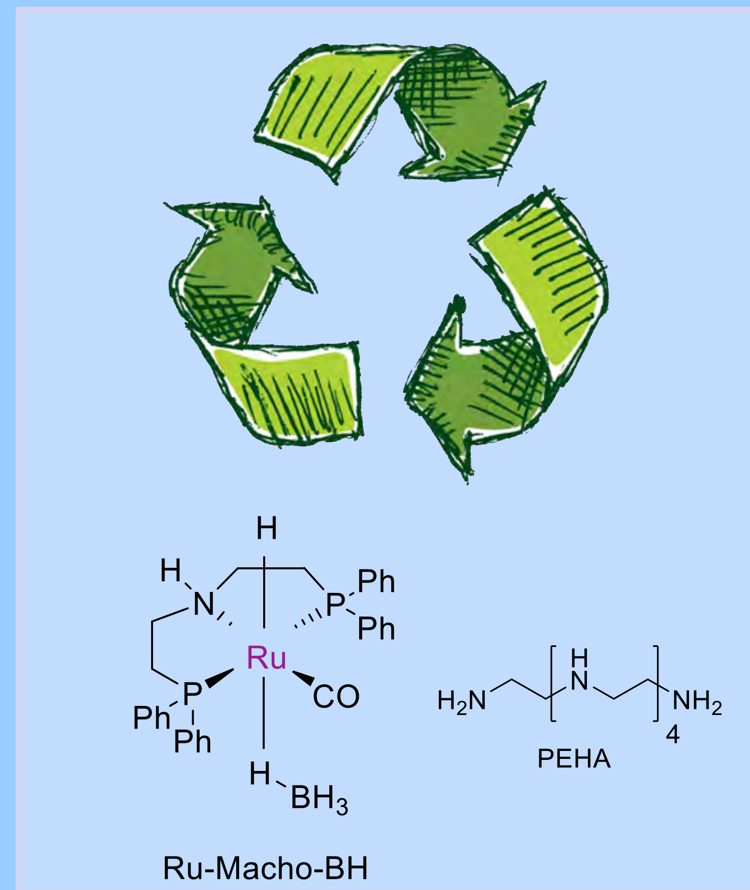
[Mn] =



Kar, S.; Goeppert, A.; Kothandaraman, J.; Prakash, G. K. S. *ACS Catal.* **2017**, *7 (9),* 6347-6351.



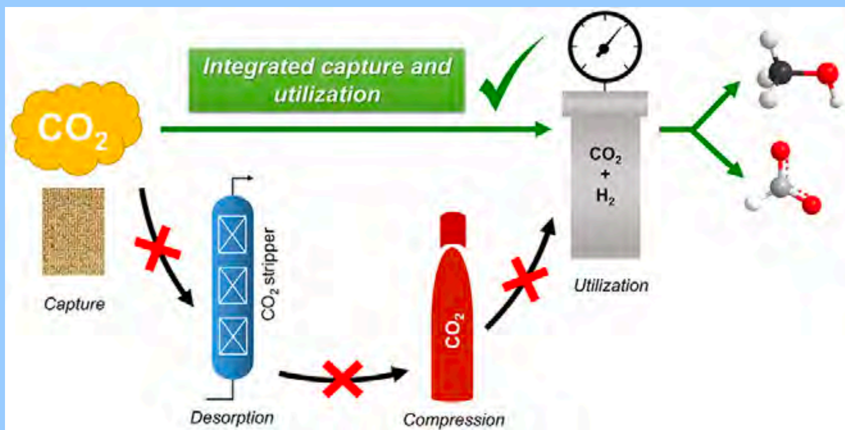


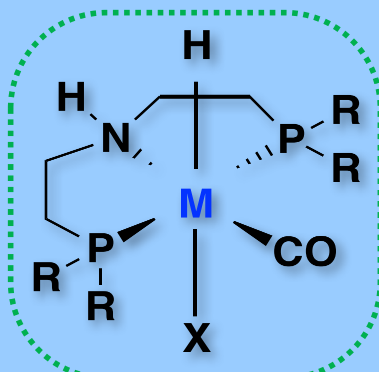


S. Kar, R. Sen, A. Goeppert and G. K. S. Prakash, *J. Am. Chem. Soc.*, **2018,** *140,* 1580-1583.

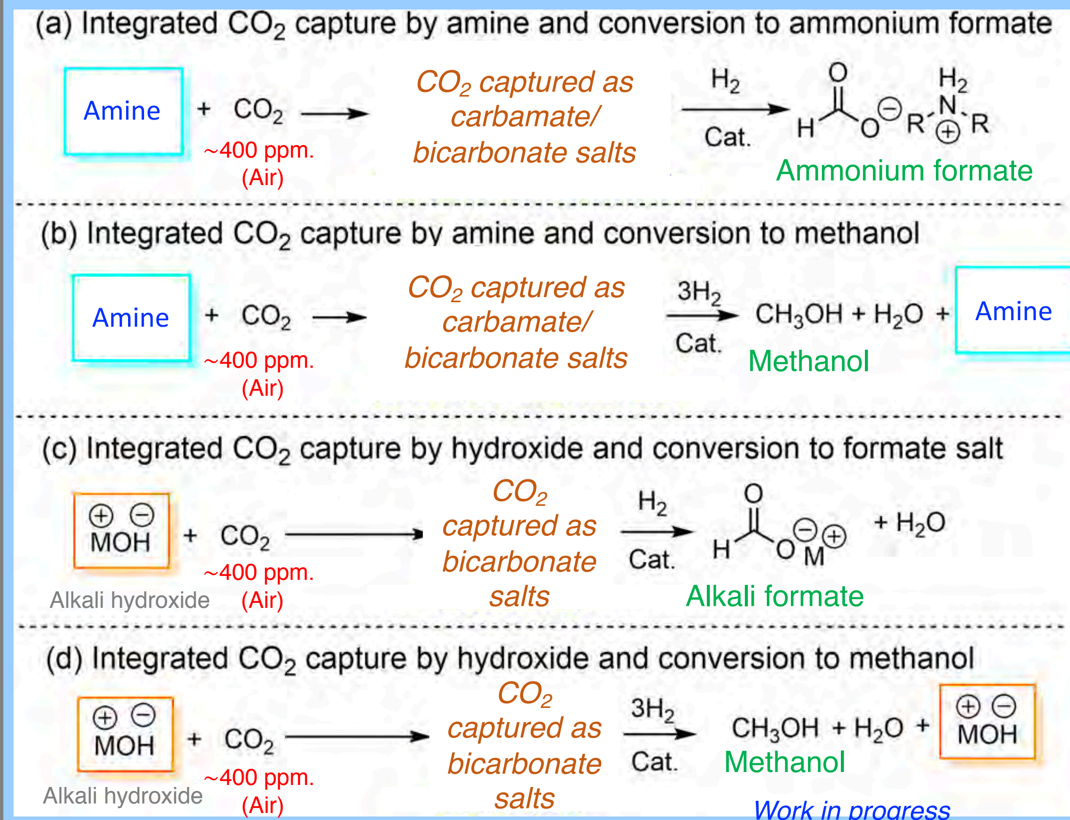
Integrated CO_2 Capture and Conversion Systems

A Carbon Neutral Cycle



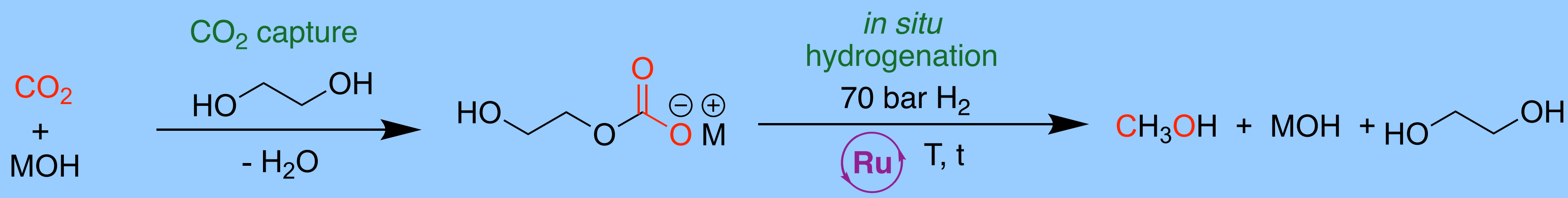


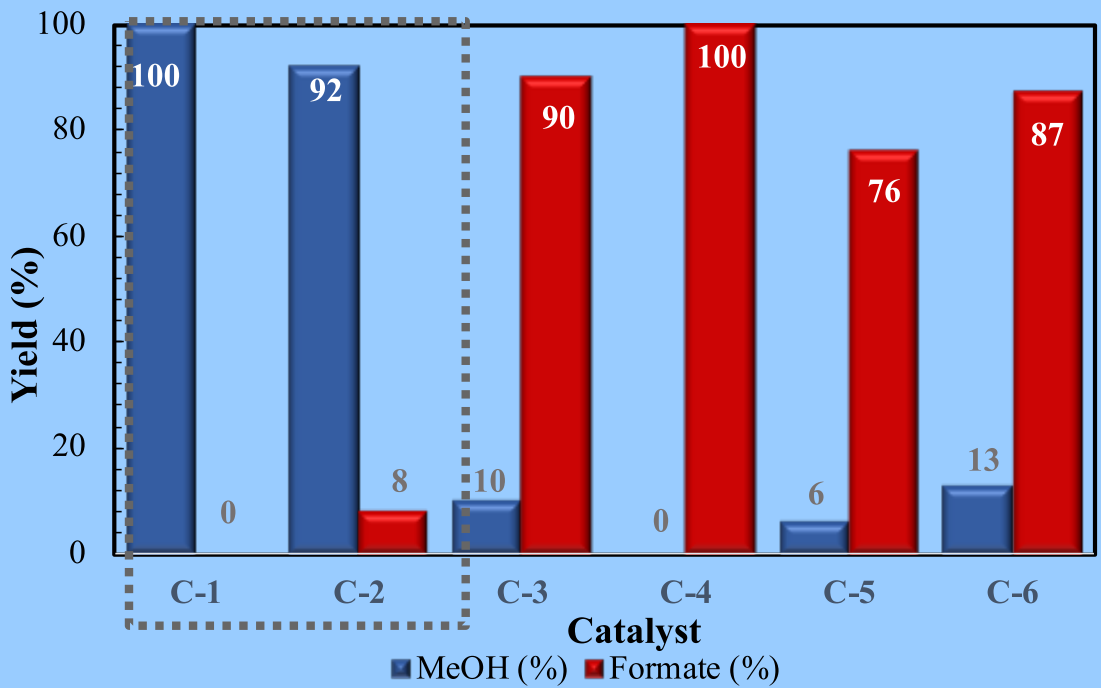
M = Ru, Fe, Mn
R = Ph, *i*Pr, *t*Bu, Cy
X = Cl, Br, H-BH_3

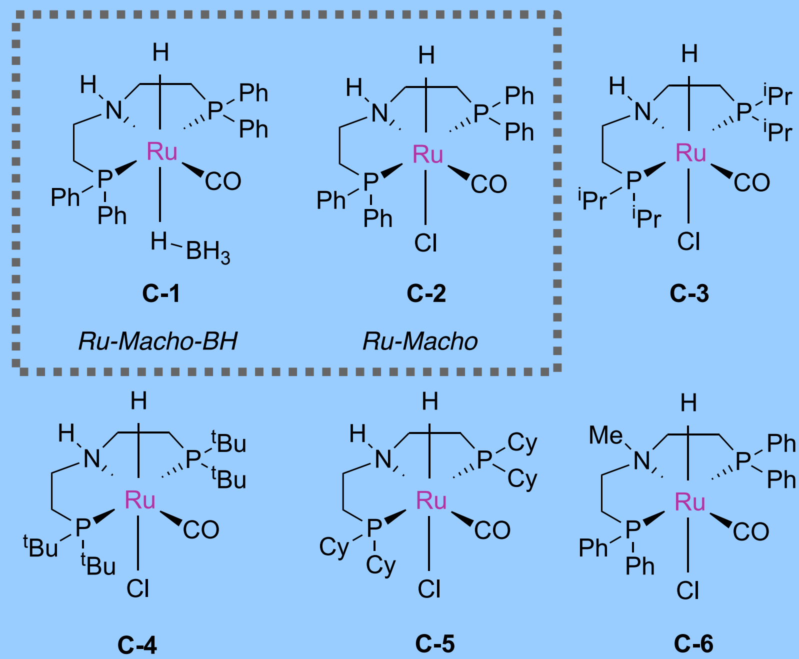


(a) *Acc. Chem. Res.* **2019**, Articles ASAP ; (b) *J. Am. Chem. Soc.* **2019**, *141* (7), 3160-3170; (c) *J. Am. Chem. Soc.* **2018**, *140* (49), 16873-16876; (d) *J. Am. Chem. Soc.* **2018**, *140* (5), 1580-1583; (e) *Green Chem.* **2016,** *18* (21), 5831-5838; (f) *J. Am. Chem. Soc.* **2016**, *138* (3) 778-781.

Tandem Hydrogenation of Captured CO_2 in ethylene glycol

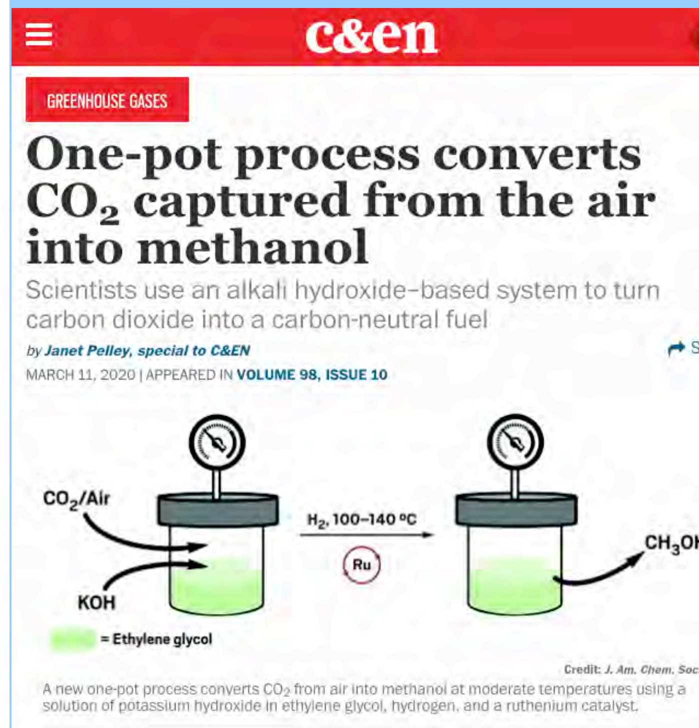






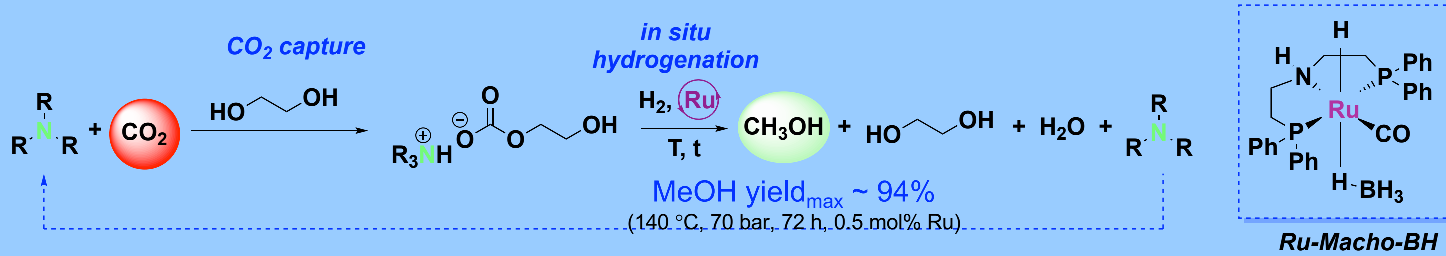
- Amine-free system for integrated CO_2 capture and conversion to methanol has been developed.
- Ethylene glycol + KOH mediates the hydrogenation of the captured CO_2 most efficiently.
- Low temperature regeneration of hydroxide base has been demonstrated.
- The partial loss of the hydroxide is due to in-situ formation of carboxylates from the solvent alcohol.

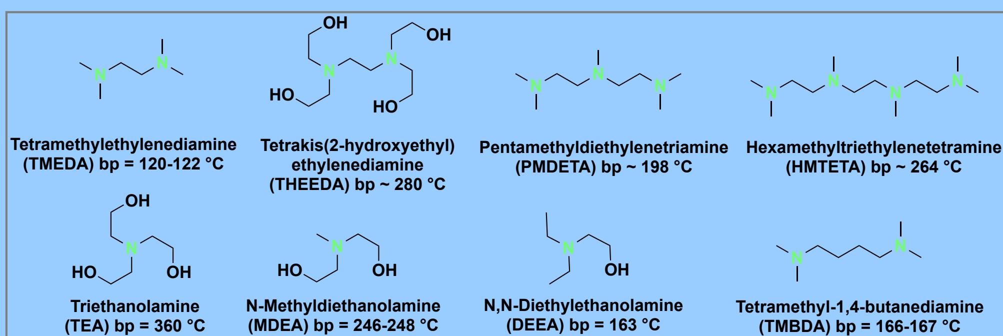
J. Am. Chem. Soc. 2020, *142*, 10, 4544–4549.



https://cen.acs.org/environment/greenhouse-gases/One-pot-process-converts-CO_2/98/i10

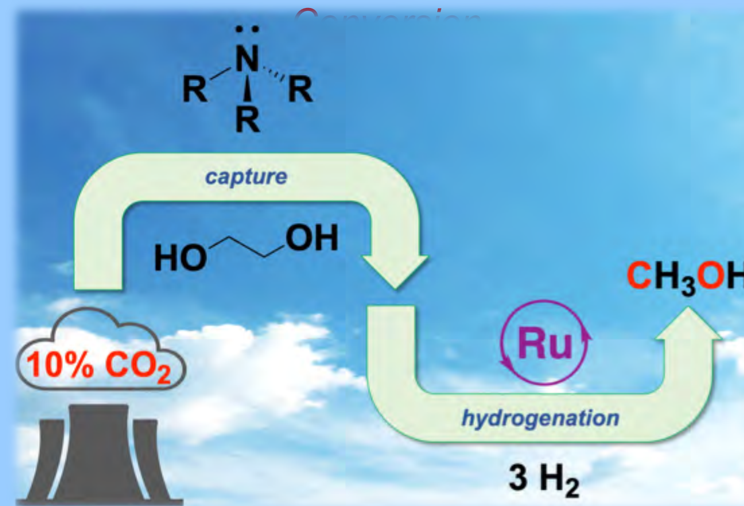
Turning Flue gas into Fuel: Tertiary Amine Based Integrated CO_2 Capture and Conversion to Methanol





- ✓ offers enhanced stability (*vs. primary/secondary amines*)
- ✓ minimized deactivating side reactions (*vs. hydroxide bases*)

Post-Combustion CO_2 Capture and Conversion

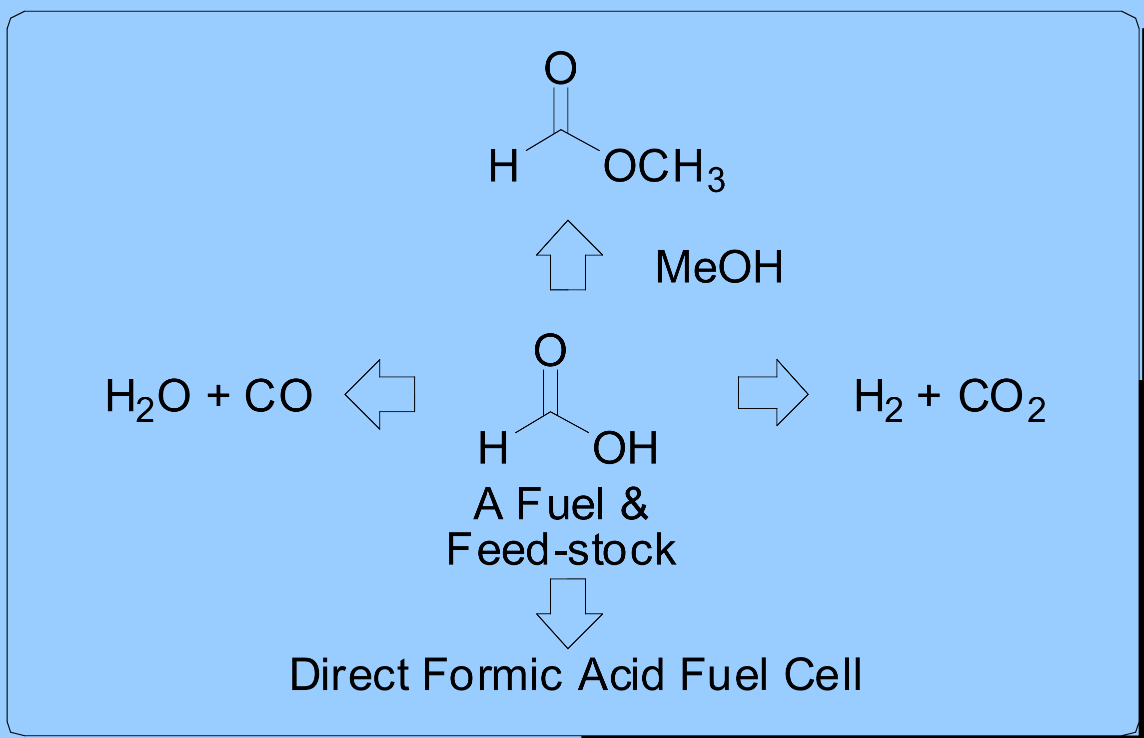


Sen, R.; Koch, C. J.; Goeppert, A.; Prakash, G. K. S., Tertiary Amine-Ethylene Glycol Based Tandem CO_2 Capture and Hydrogenation to Methanol: Direct Utilization of Post-Combustion CO_2 ***ChemSusChem* 2020**, DOI: 0.1002/cssc.202002285

Electrochemical Reduction of CO_2 to Syngas and Formic Acid

Standard Electrochemical Reduction Potentials of CO_2 at pH=7, NHE, NTP Conditions

$CO_2 + e^- \longrightarrow CO_2^{\bullet -}$	$E^o = -1.96\ V$	(1)
$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$	$E^o = -0.53\ V$	(2)
$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$	$E^o = -0.61\ V$	(3)
$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O$	$E^o = -0.48\ V$	(4)
$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$	$E^o = -0.38\ V$	(5)
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$	$E^o = -0.24\ V$	(6)



Methanol from CO_2

imitating nature

Sources of carbon dioxide:

•Industrial flue gases: Fossil fuel burning power plants, steel and cement factories, etc.

•The atmosphere itself (400 ppm)

Hydrogenation of CO_2

$$CO_2 + 3H_2 \xrightleftharpoons{\text{Cu/ZnO}} CH_3OH + H_2O$$

Electrochemical reduction of CO_2

$$CO_2 + 2H_2O \xrightarrow[\text{Electrode catalyst}]{\text{Electrons}} [CO + 2H_2] + 3/2\ O_2$$

$$[CO + 2H_2] \longrightarrow CH_3OH$$

Electricity needed to produce hydrogen or for the reduction can come from any renewable (wind, solar, etc.) or nuclear energy source

US Patent, 7,704,369, April 27, 2010

Water Electrolysis

H_2O + electricity ⟶ $H_2 + 1/2\ O_2$

39.4 kWh/kg H_2 needed at 100 % theoretical efficiency
In practice closer to 50 kWh/kg H_2

At 4 ¢/kWh the cost to produce H_2 is about $2.6 /kg

➡ Main driver is cost of electricity
Capital and operating costs are a minor part of the cost

CO_2	+	H_2	⟶	CH_3OH	+	H_2O
1.375 kg		0.188 kg		1 kg		0.563 kg

At 4 ¢/kWh the cost of producing methanol is estimated to be about $0.5 /kg or $1.8 per gallon

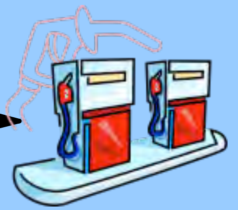
New Photochemical Processes are also being developed to split water

Geothermal methanol from CO_2

CRI Carbon Recycling International

"George Olah CO_2 to Renewable Methanol Plant"
HS Orka Svartsengi Geothermal Power Plant, Iceland
Production Capacity: 12 t/day

$$\text{geothermal } CO_2 + 3H_2 \longrightarrow H_2O + CH_3OH \longrightarrow$$



$3/2\ O_2$ ← $3H_2O$ ↑ electrolysis using geothermal energy

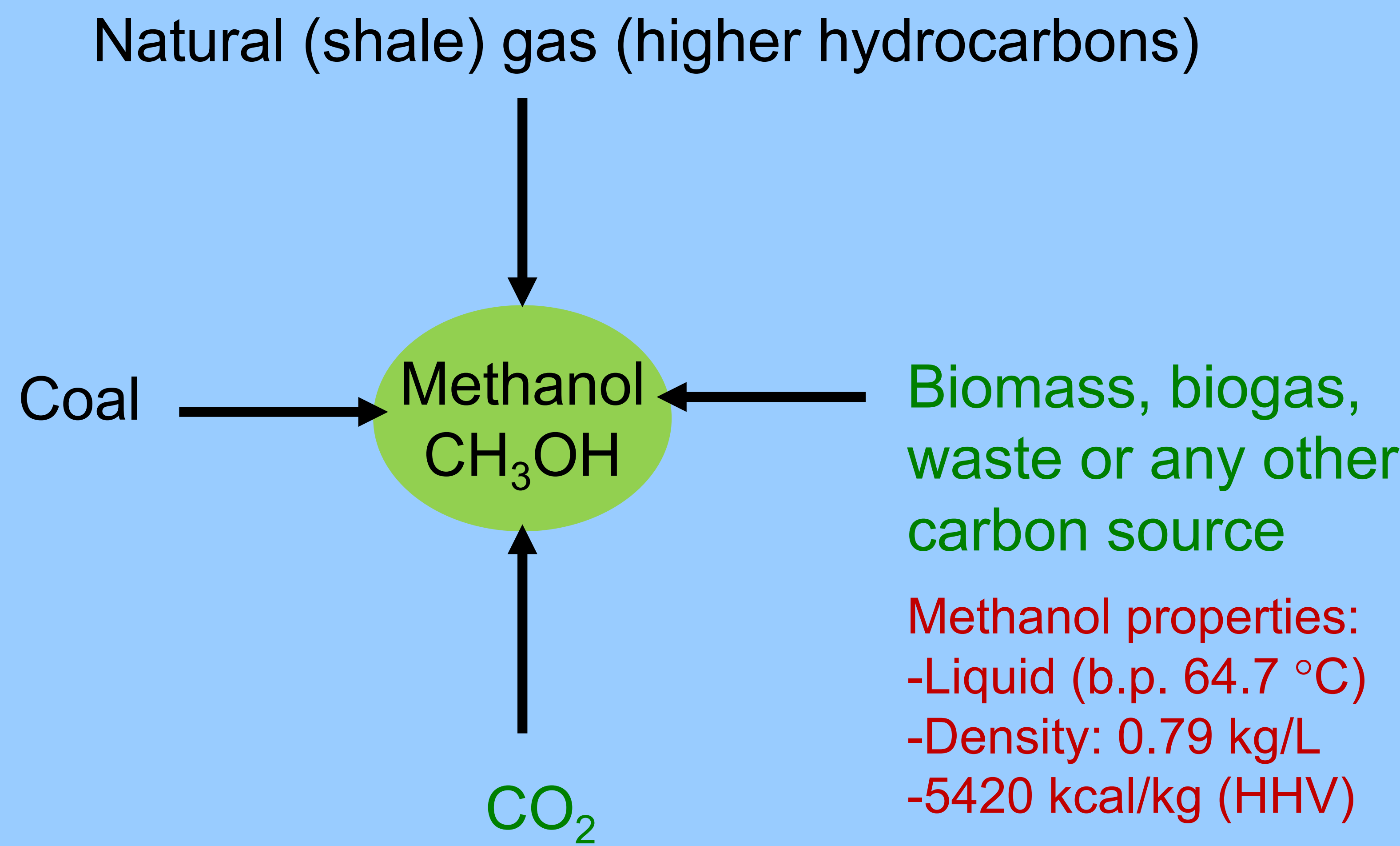
Geothermal methanol sold under the name "Vulcanol"

Electricity cost ~ 1-2 ¢/kWh

> 90% reduction in CO_2 emissions compared to gasoline

About 40 kWh are needed to produce a gallon of methanol (11 kWh/L),
Methanex and Geely are the major share holders

Ubiquitous methanol, a fuel and feedstock!



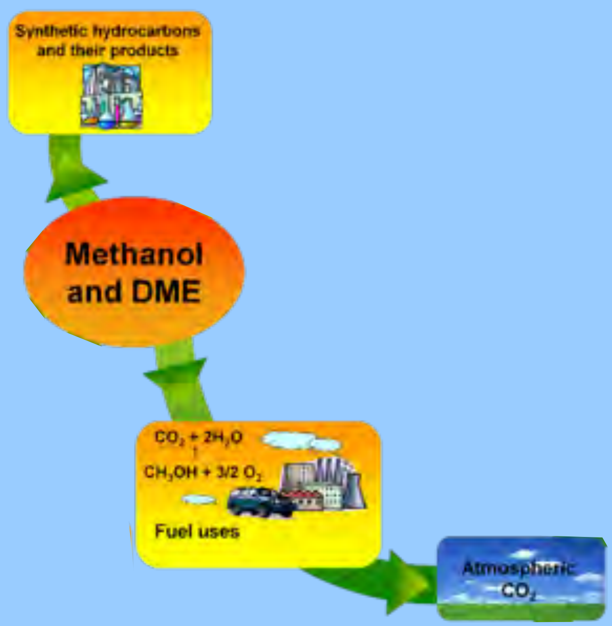
Methanol properties:
-Liquid (b.p. 64.7 °C)
-Density: 0.79 kg/L
-5420 kcal/kg (HHV)

$CH_3OH \longrightarrow CH_3OCH_3$ Dimethylether (DME)

KISS Principle, Bridge fuel in the short term and
Renewable Carbon Neutral Fuel in the long term!

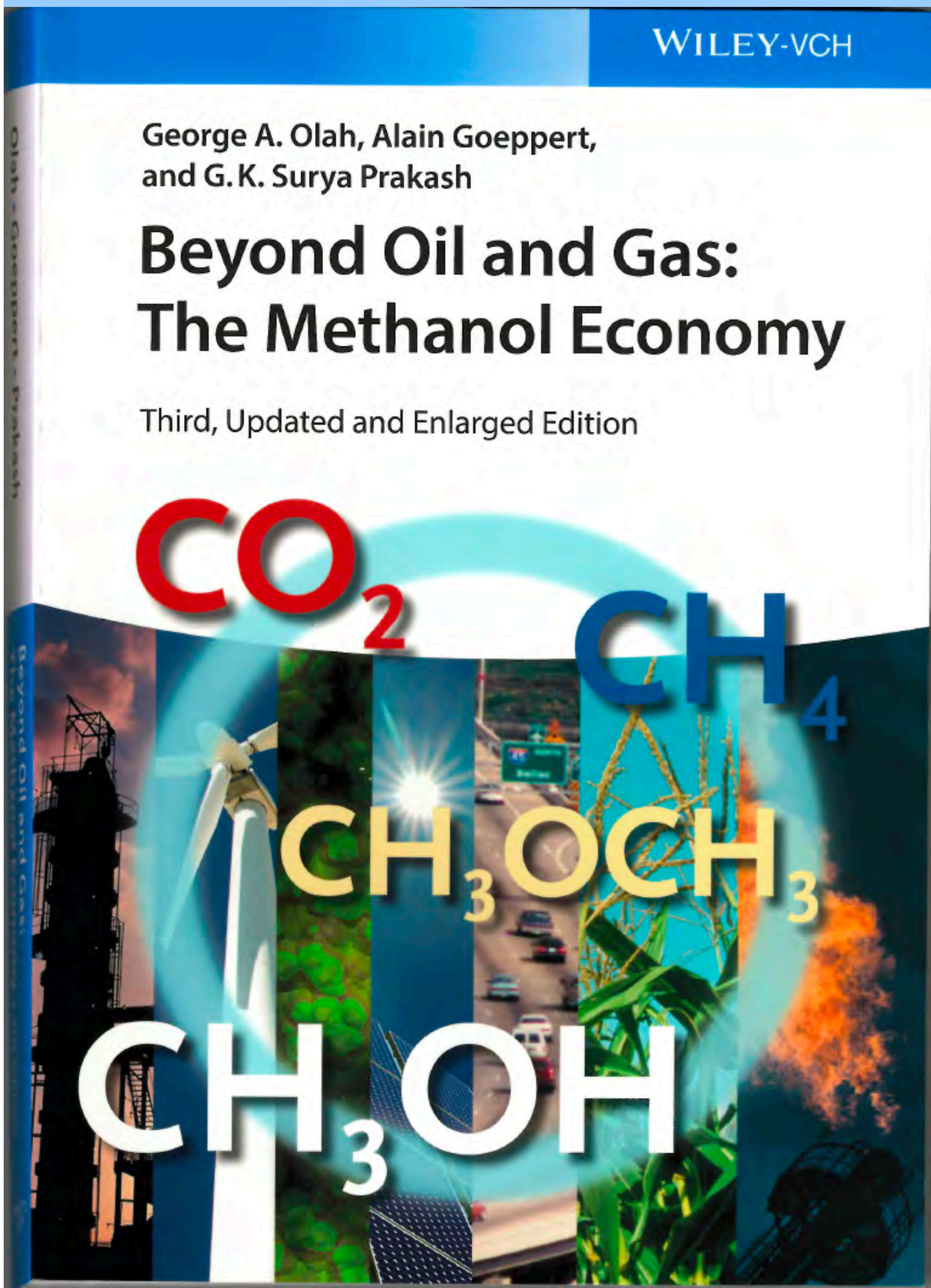
For the one Carbon (CO_2) Problem, one Carbon (CH_3OH) Solution!

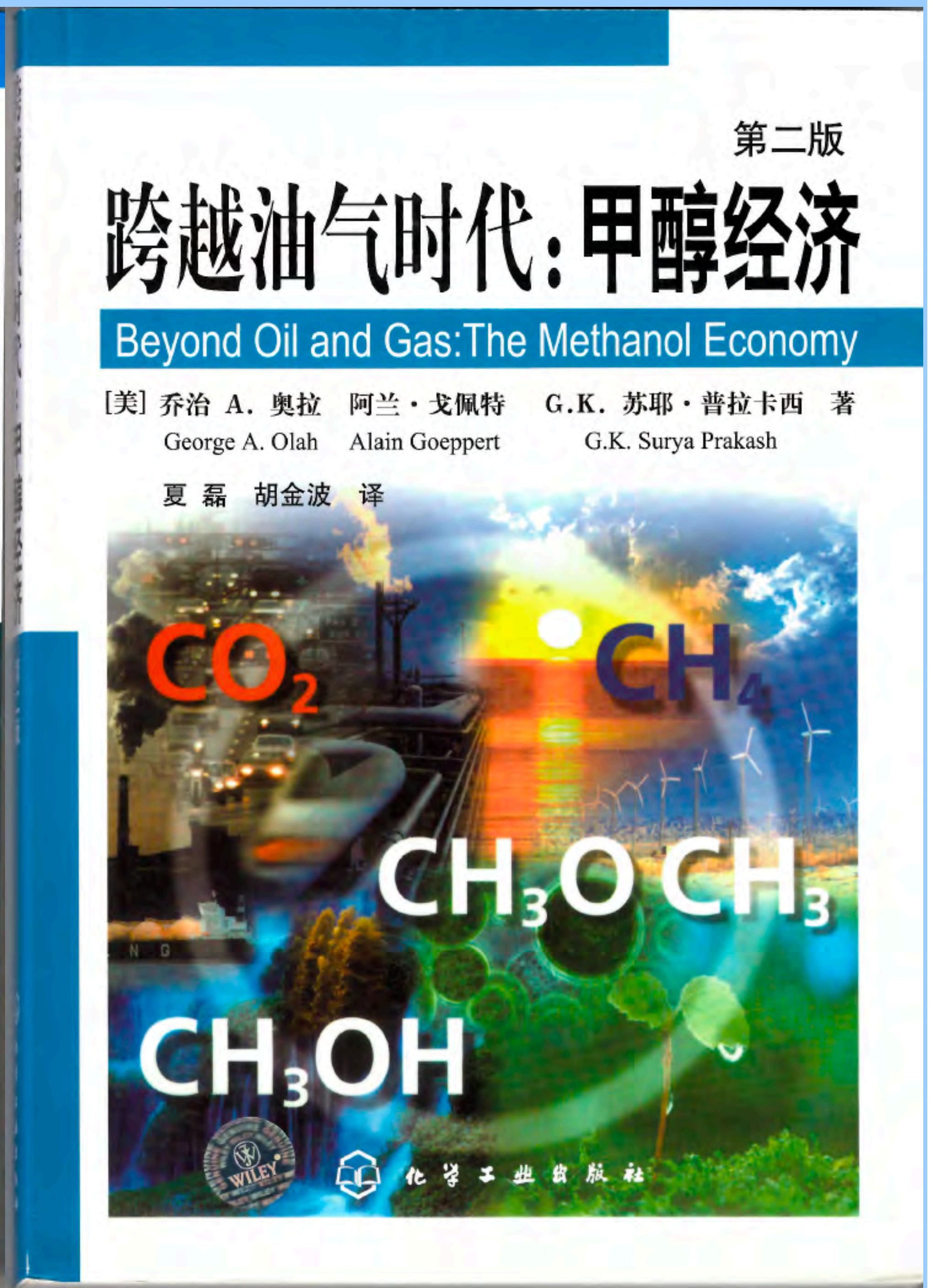
Utilization and recycling of CO_2 from the air
Anthropogenic carbon cycle
Mimic Nature's photosynthetic cycle



"Methanol Economy"

Sustainable recycling of atmospheric CO_2 to fuels and materials


WILEY-VCH
George A. Olah, Alain Goeppert,
and G.K. Surya Prakash
Beyond Oil and Gas:
The Methanol Economy
Third, Updated and Enlarged Edition
CO2
CH4
CH3OCH3
CH3OH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Beyond Oil and Gas:The Methanol Economy
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George A. Olah Alain Goeppert G.K. Surya Prakash
夏 磊 胡金波 译
CO2
CH4
CH3OCH3
CH3OH
WILEY
化学工业出版社

Methanol-Fueled Cars Could Drive Us Toward an Emissionless Future
Jean Kumagai

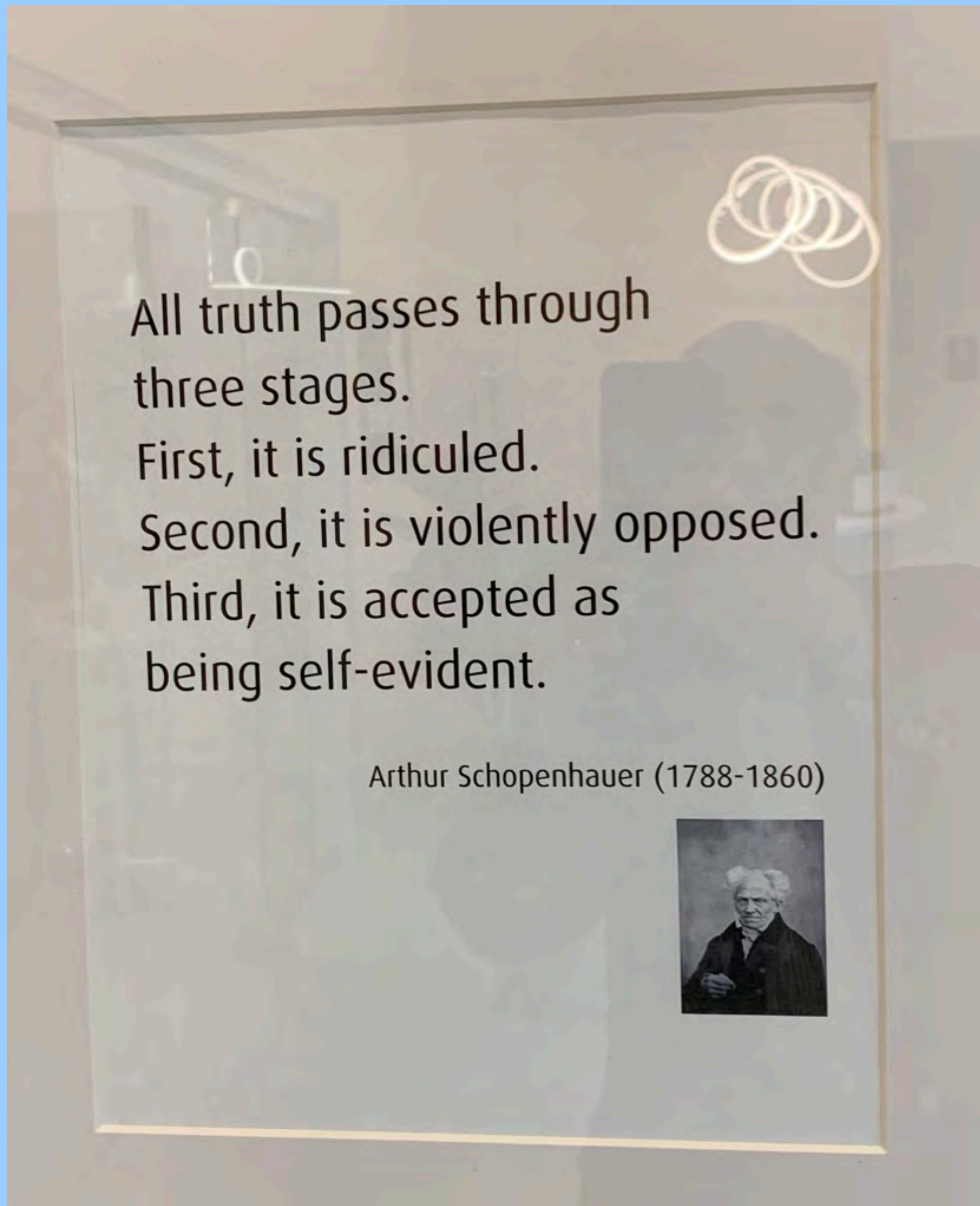
“Right now, the world is still flush with fossil fuel resources,” says USC’s Prakash. Absent a strong system of rewards and penalties that discourages the use of those resources, people will use them. Methanol offers a bridge from our highly carbonated present to a low-carbon future, in which electricity comes from renewables or nuclear and cars are electric. In the meantime, Prakash says, methanol can help. Rather than wastefully flaring natural gas in the Bakken Formation, for instance, why not place a methanol plant there and produce fuel? Rather than curtailing wind and solar when the power grid can’t absorb their output, why not use the excess for methanol?

“Methanol gives us a way to store not just kilowatt- or megawatt-hours of power but gigawatt-hours,” Prakash says. “It could be a game changer.”

IEE Spectrum Magazine, June **2018** Issue

“Americans will do the right thing in the end after exhausting all other alternatives”

Sir Winston Leonard Spencer-Churchill


All truth passes through
three stages.
First, it is ridiculed.
Second, it is violently opposed.
Third, it is accepted as
being self-evident.
Arthur Schopenhauer (1788-1860)

Acknowledgments

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Amanda Baxter
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ARPA-E, STAQ Energy
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Inaugural 2013 $ 1 Million Eric and Sheila Samson Prime Minister's Prize for Alternatives to Transportation Fuels from Israel (shared with the late Prof. Olah)