The Methanol Economy[R]

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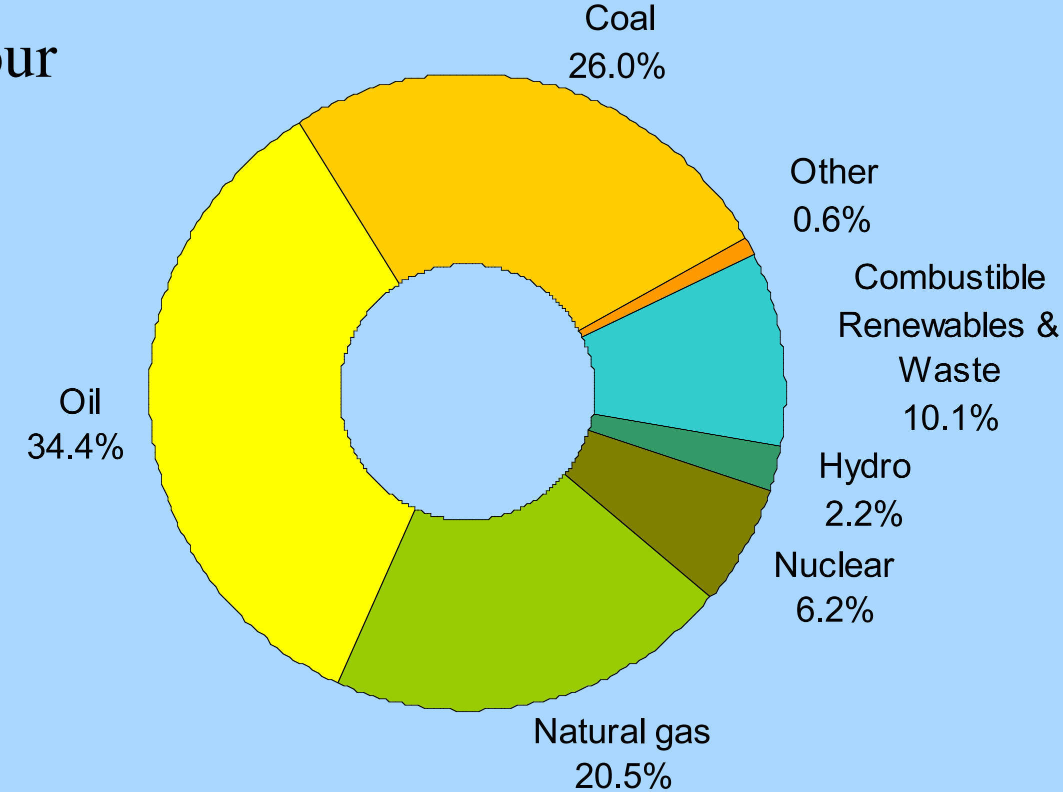
Increasing world population
Increase in standard of living

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). 401 ppm

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



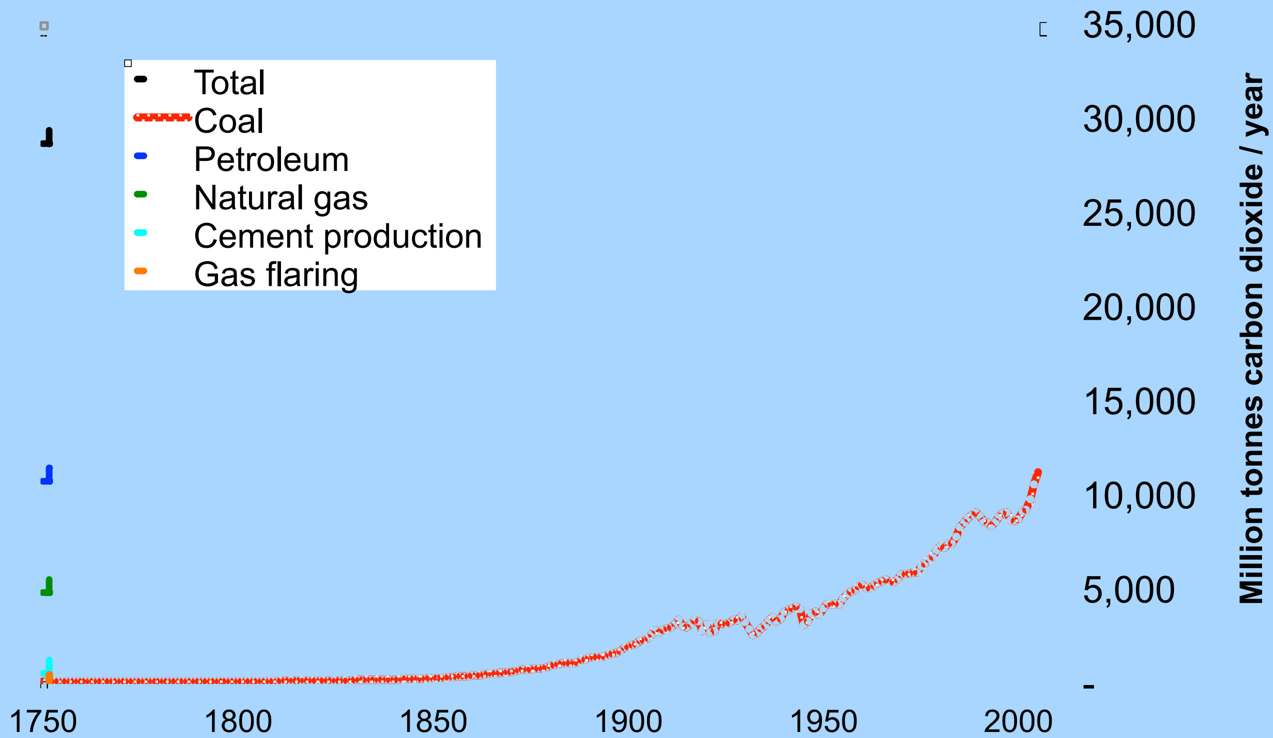
Total 11 741 Mtoe

Distribution of the World Total Primary Energy Supply in 2006.

Based on data from the International Energy Agency (IEA)

Key World Energy Statistics 2008

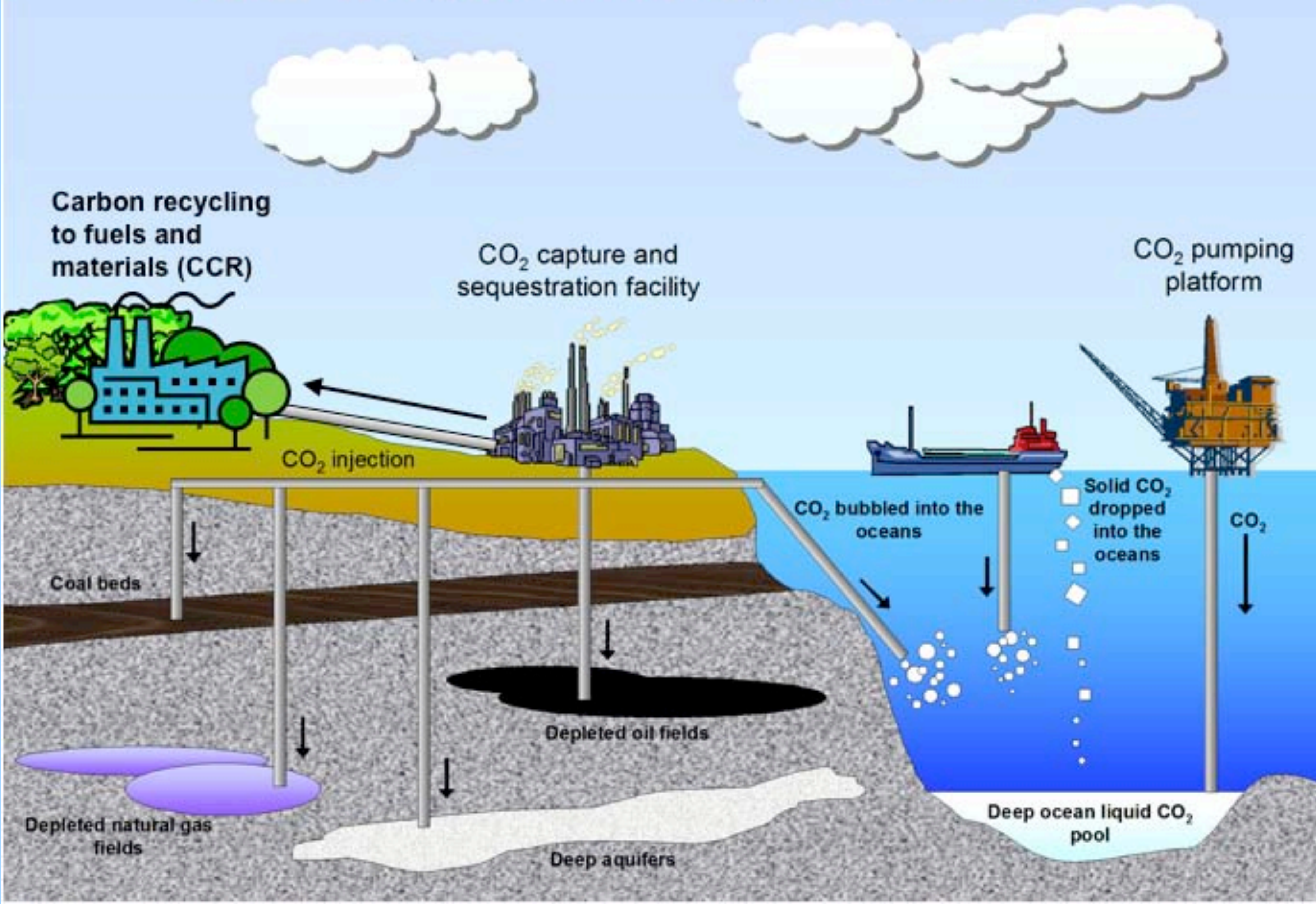
Annual Global CO_2 Emissions- 1750-2005



More than 30 billion tonnes of CO_2 per year released into the atmosphere!

About half the CO_2 emissions accumulate in the atmosphere. Presently, > 15 billion tonnes per year. Rest in the Oceans. Ocean Acidification is a Bigger Problem!

Carbon capture and sequestration (CCS)



Daily usage of fossil fuels

❖85 Million Barrels of Oil is consumed!

❖8.4 Billion m^3 of Natural Gas

❖16 Million Tonnes of Coal

> 30 billion tonnes of CO_2 released into the atmosphere per year
Contributing to greenhouse effect – Global Warming

Ethanol economy: in the US, 14. 9 billion gallons of ethanol is produced per year (~353 million barrels) from corn. Equivalent to 225 million barrels of oil: 2.7 days supply!

In Brazil, ~ 6.84 billion gallons of ethanol from sugar cane is produced.

Biodiesel a lot smaller: requires more land.

Biomass

CO_2 fixation by photosynthesis (carbon neutral)

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))

* Processing technologies, energy use

* Overall energy balance

Sun is the source of most energy on Earth- **past, present and future**
130,000 TW continuous- A reliable nuclear fusion reactor!

Alternative Energies?




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
- Fossil fuels are still the biggest bargain
- Most renewable energies are intermittent
-They produce mostly electricity
- Difficult to store
(storage in the form of Hydrogen, methanol, etc)



Hydrogen Economy

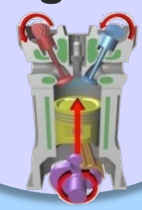
Hydrogen economy (clean fuels, fuel cells)

- 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

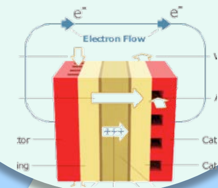
The Methanol Economy: Methanol as a fuel and feed-stock

In Internal Combustion Engines



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

In Direct Methanol Fuel Cells



Conversion to olefins-gasoline, diesel, etc.

Dimethyl Ether (Diesel and Household Fuel)

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

CH_3OH

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 ^{o}C).

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

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

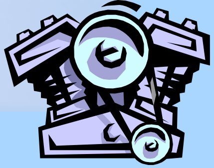
❖Half the volumetric energy content of gasoline (15.8 MJ/liter), but more efficient and cleaner burning.

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

❖ Can be blended into MEG (methanol, ethanol and gasoline) Fuels

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

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 engine- air cooled engines
- ❖ Safer fuel in fires than gasoline

- ❖ Methanol burns better, cleaner emissions, less NOx and particulates
- ❖ Methanol can be dispensed in regular gas station requiring only limited modifications
- ❖ Compatible with hybrid (fuel/electric) system
- ❖ New Generation Spark-Ignition Heavy Duty Engines (40% smaller than the Diesel Engines)

Diesel-Like Efficiency And Torque (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

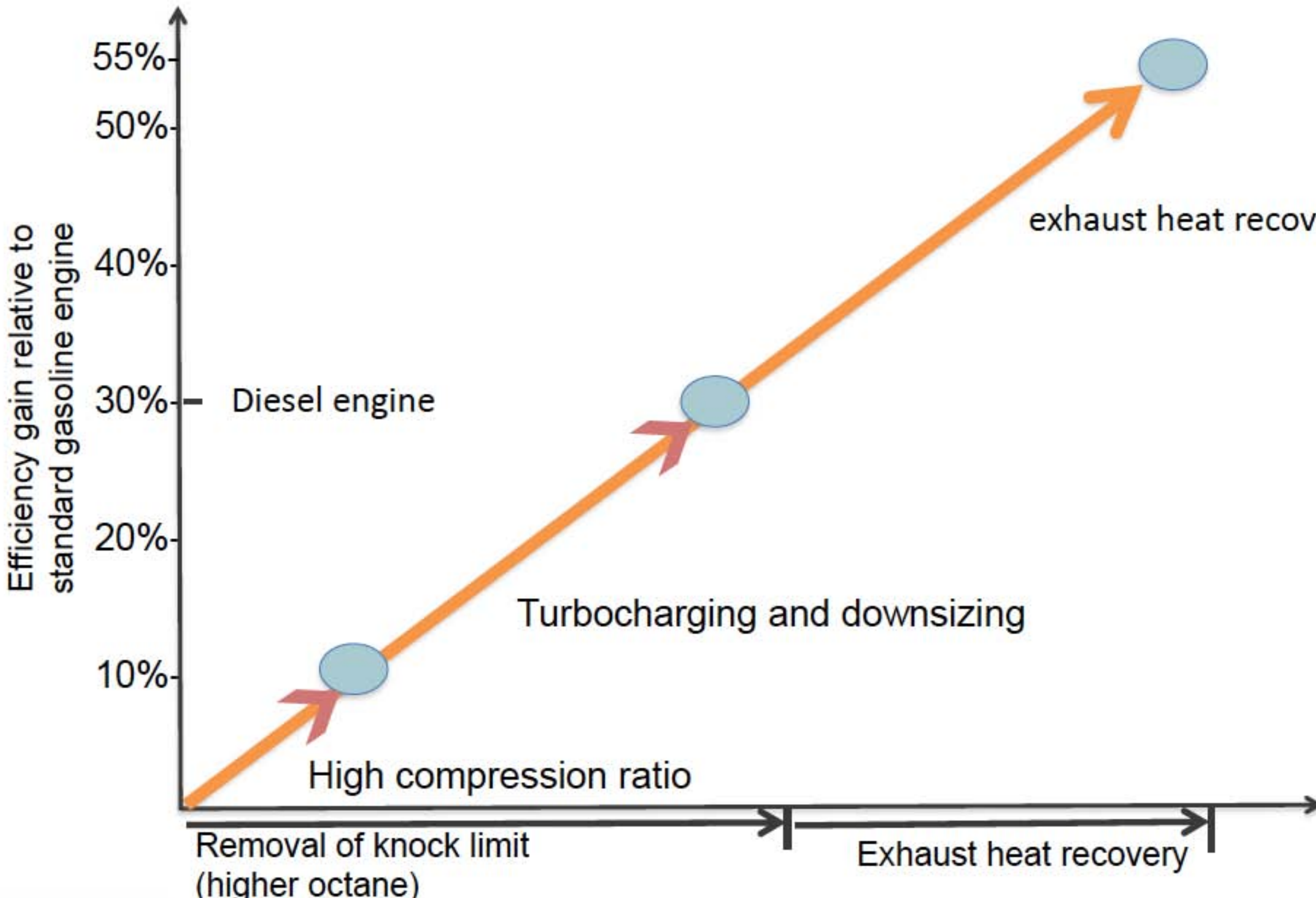
- Spark ignition methanol engine could provide around 1.5 X more torque/liter than diesel

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

	Diesel	Methanol Engine size (liter)
	9	**9**
Torque (lb-ft)	1300	2000

Size of diesel engine with same torque as methanol engine 15 liter

Super -efficient Spark Ignition Methanol Engines



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 as a marine fuel

Availability, distribution and storage

Engine technology and adjustment to the ship

Environment and cost benefit

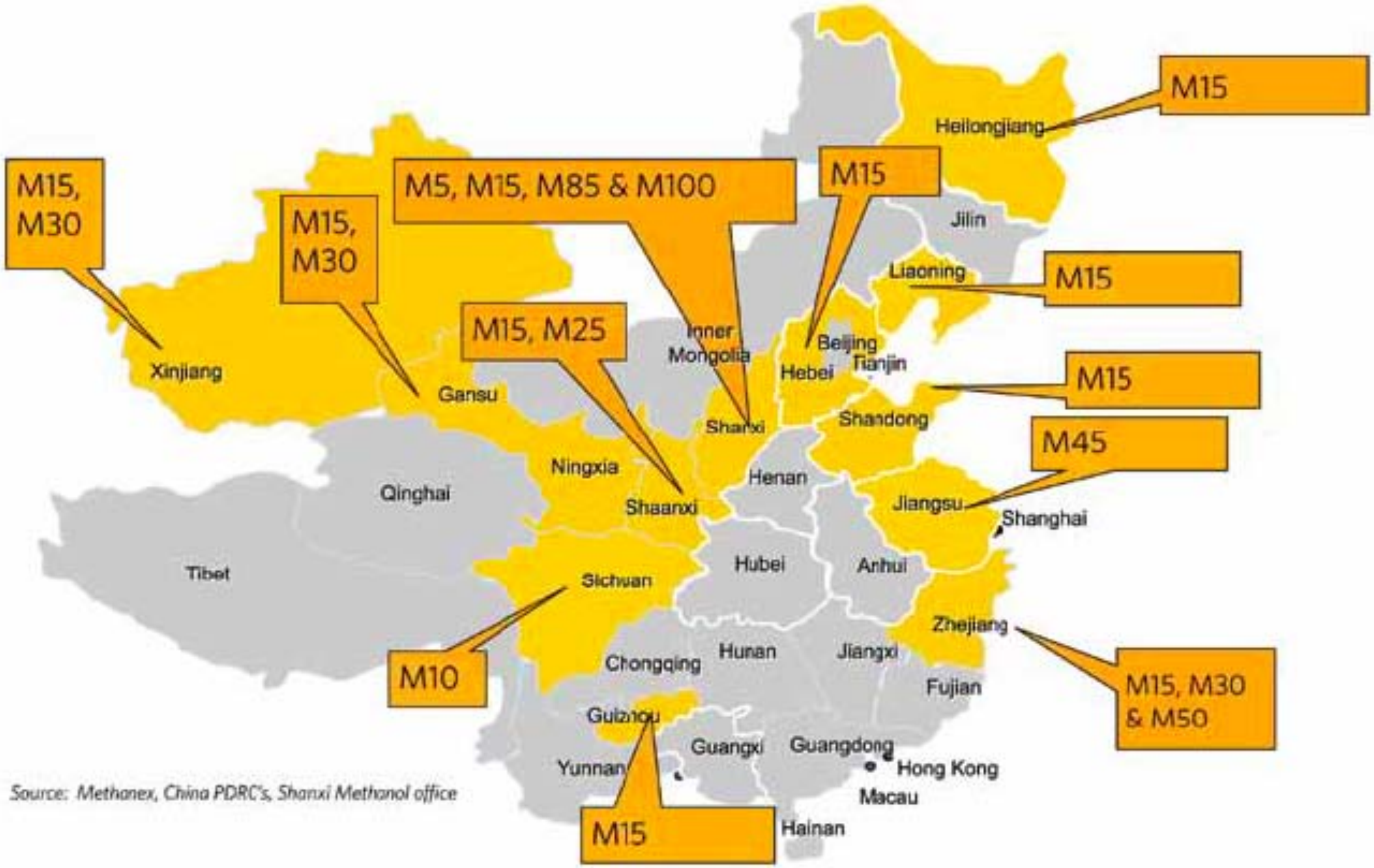
Safety and regulations

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

Wärtsilä Engine with a total of 32,000 horsepower!

WELCOME ONBOARD A GREENER JOURNEY!

- Stena Germanica – the world's first methanol ferry



Source: Methanex, China PDRC's, Shanxi Methanol office

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) and very clean burning
- ❖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 is selling DME Trucks!

Advanced methanol-powered fuel cells by Reforming

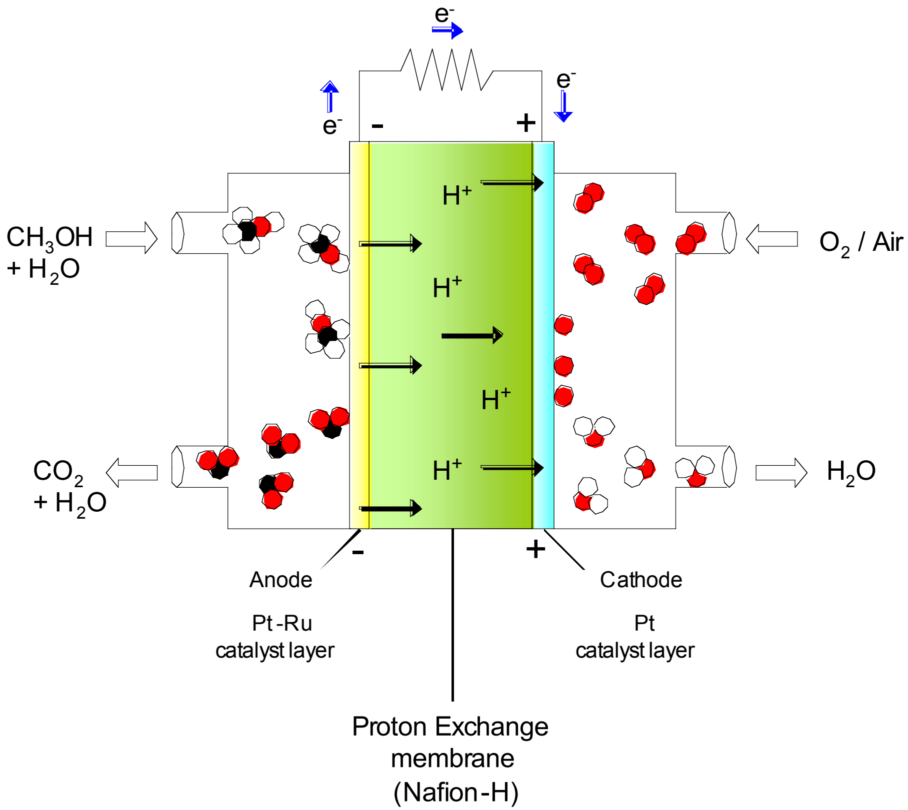
On-board generation of hydrogen through methanol reforming

$CH_3OH + H_2O$ → Reforming Catalyst → $H_2 + CO_2$ → 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)

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:

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

$$E_{cell} = 1.214\ V$$

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

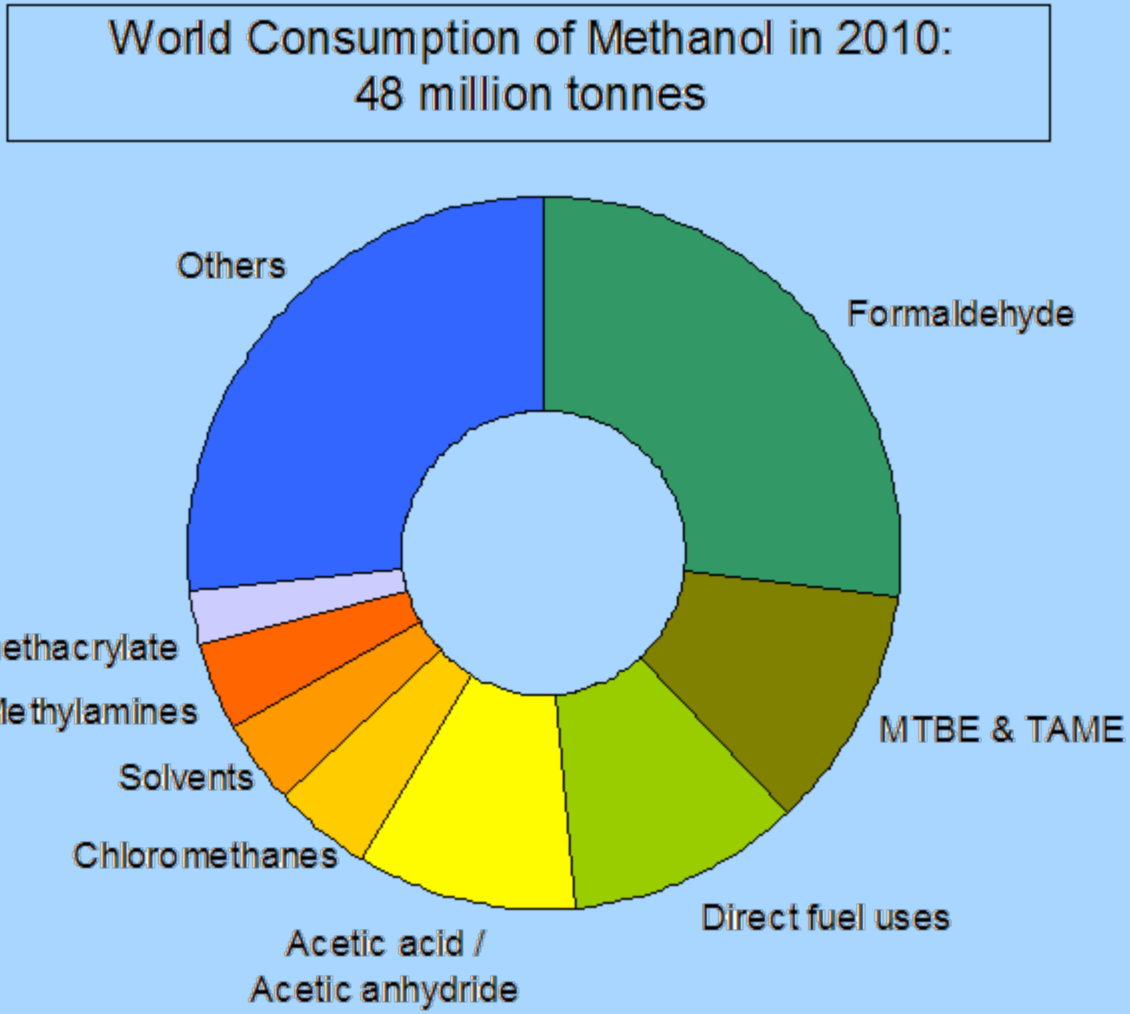
Methanol as a fuel and feedstock

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

* **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 cooking fuel in developing countries**
Much cleaner burning and efficient than wood

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



MTBE: Methyl *tert*-butyl ether
TAME: Tertiary-amyl methyl ether

Source: SRI Consulting

Current World Production ~75 M tonnes (PRC, 58%)

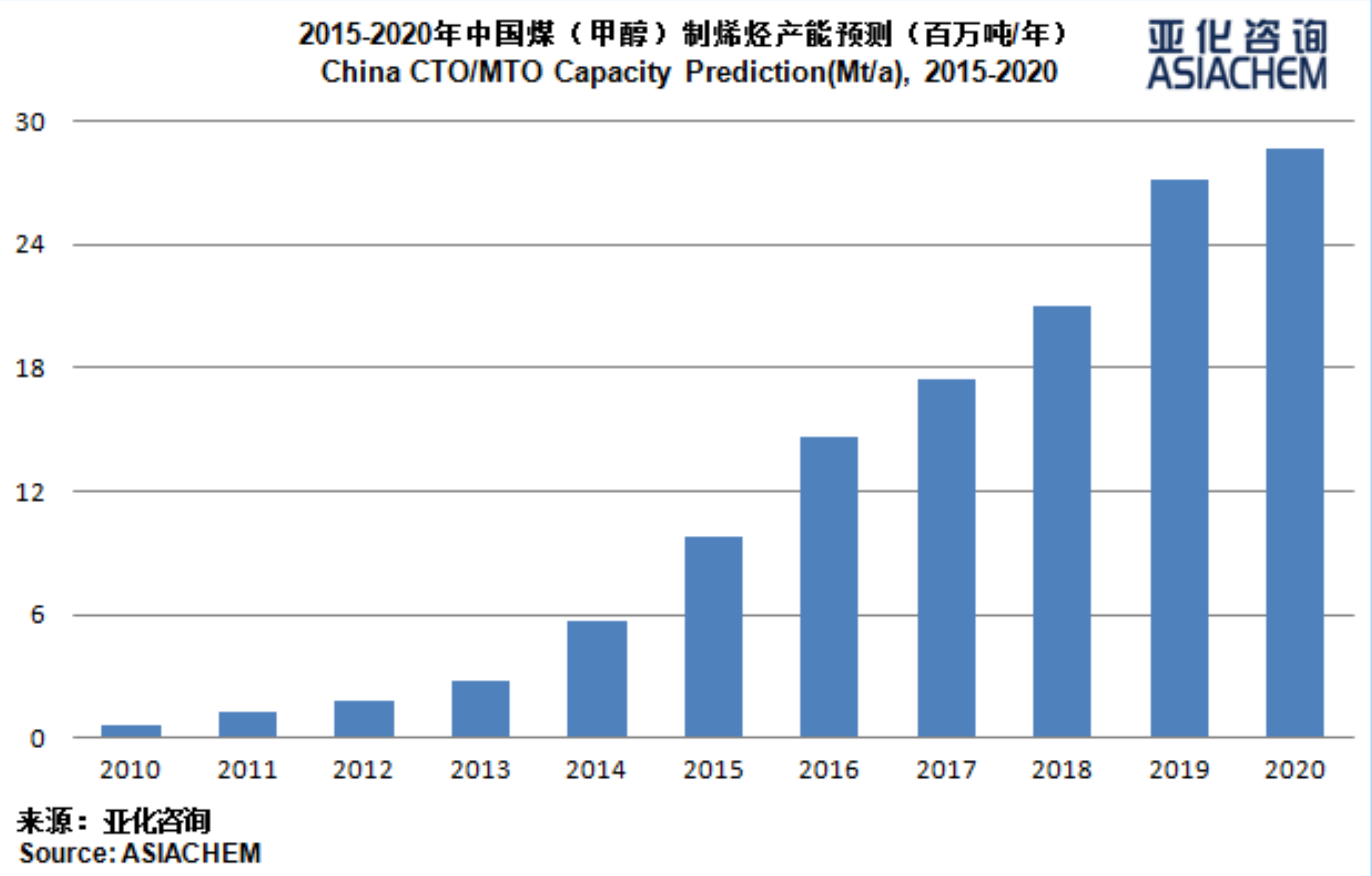
METHANOL AS HYDROCARBON SOURCE

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

$$\downarrow$$

HYDROCARBON FUELS AND PRODUCTS

(Gasoline, Diesel, etc.)


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

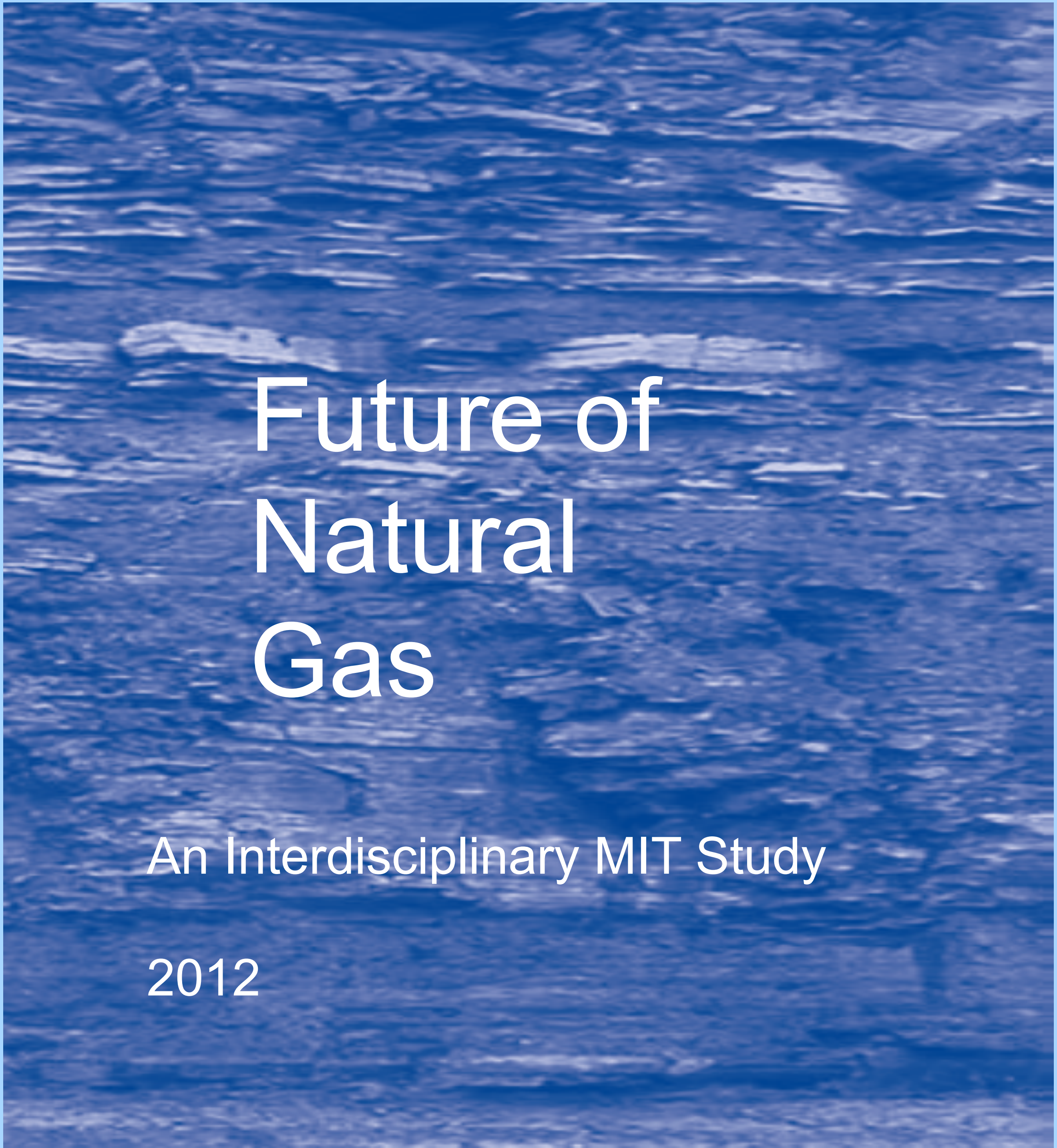
Biomass Gasification

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

FINDINGS

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)**

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

Excess H_2 generally used for ammonia (NH_3) production

S=3

- **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)**

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

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

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

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

CH_3OH from coal
A proven technology

$$3\,C + H_2O + O_2 \longrightarrow 3\,CO + H_2$$

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

$$C + H_2O \longrightarrow CO + H_2$$

China is currently adopting this approach on a massive scale based on its large coal reserves
100 plants in construction or planned!

1 ton of Methanol from 1.42 – 1.59 tons of coal

Due to the low H/C ratio of coal: a lot of CO_2 is produced
2.37 – 3.52 tons !

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

$$\text{Biomass} \longrightarrow \underset{CO + H_2}{\text{Syn-gas}} \longrightarrow \text{Methanol}$$

•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

$\downarrow$ Fast Pyrolysis, 550 °C

Condensate + Char + Slurry, 90%

$\downarrow$ Gasification with Oxygen, 1200 °C

$CO + H_2$ Syngas, 78%

$\downarrow$

Methanol or other liquids

Bio-DME from Black Liquor

Paper manufacturing

$\downarrow$

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

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

Bio-DME filling station

Volvo DME powered truck

Bio-Methanol from Glycerol

Vegetable oil → Biodiesel production → Biodiesel

Biodiesel production → Glycerol by-product

Glycerol by-product → Syn-gas $CO + H_2$ → Methanol

BioMCN process

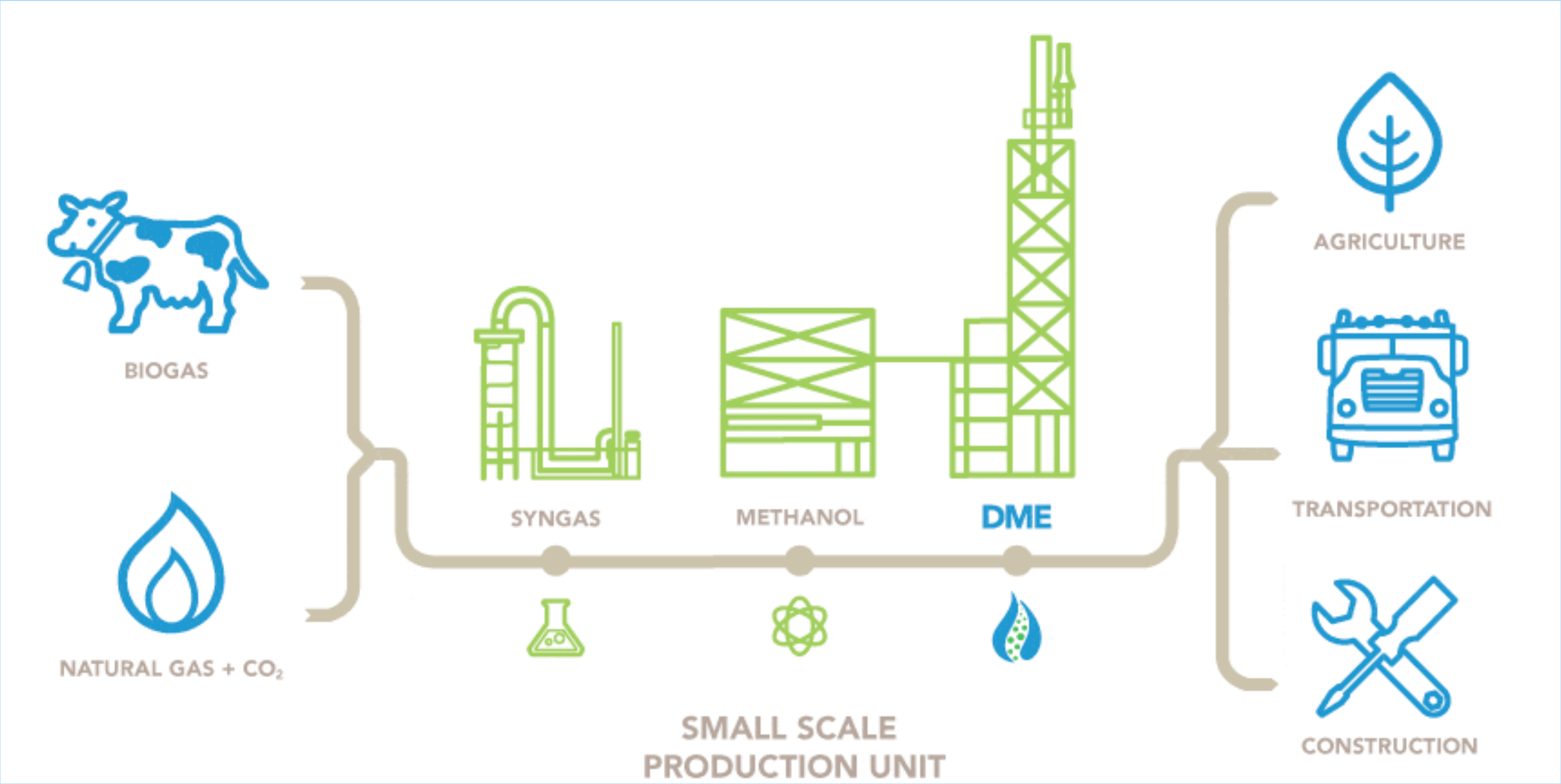
Glycerol by-product $\xrightarrow{H_2}$ Methanol

Oxford University

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

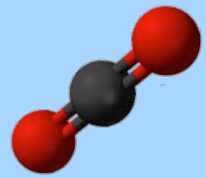
Further expansions in steps of
200 000 kT capacity planned

Oberon Fuels

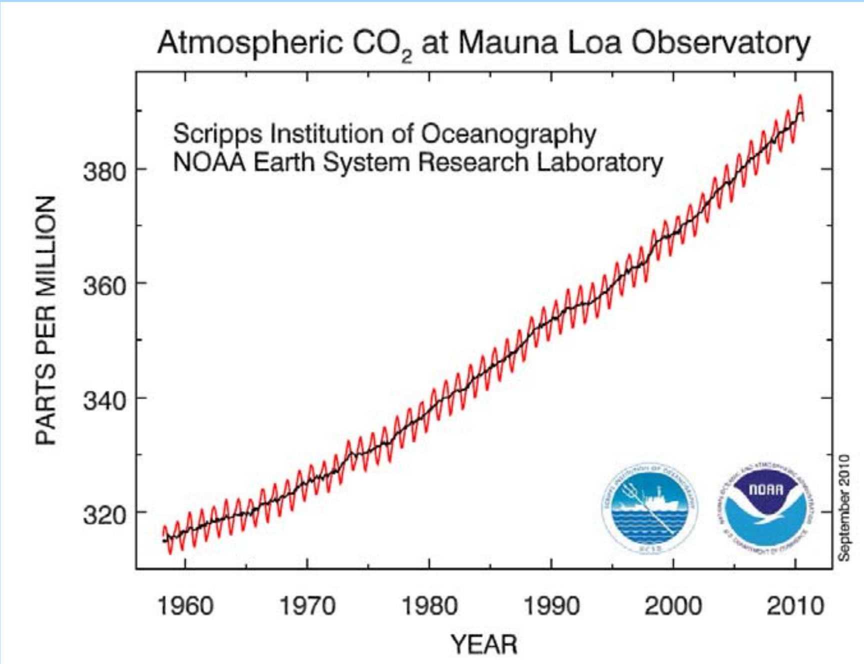


3,000 to 10,000 Gallons of Dimethyl Ether per day

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

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 (401 ppm)

Hydrogenation of CO_2

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

Heterogeneous catalysis

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

Water Electrolysis

$$H_2O + \text{electricity} \longrightarrow H_2 + 1/2\ O_2$$

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 the cost of electricity!

CO_2	+	H_2	$\longrightarrow$	CH_3OH	+	H_2O
1.375 kg		0.188 kg		1 kg		0.563 kg

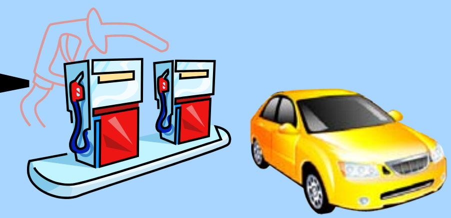
At 4 ¢/kWh the cost of producing methanol is estimated to be about $0.5 /kg or $1.8 per gallon

New Photochemical Processes are also being developed to split water

Methanol from Geothermal Sources

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

$$3H_2O \xrightarrow{\text{electrolysis using geothermal electricity}} 3H_2 + 3/2\ O_2$$



CRI Carbon Recycling International

"George Olah CO_2 to Renewable Methanol Plant"

HS Orka Svartsengi Geothermal Power Plant, Iceland

Production capacity: 11 t/day

About 40 kWh needed to produce one gallon of methanol

Electrochemical reduction of CO_2 to Syngas

Low Temperature PEM Electrolyzer

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

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

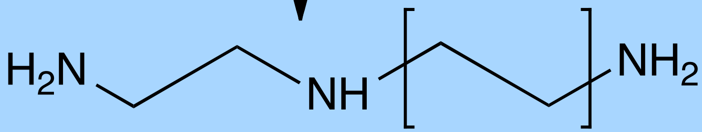
US Patent, 7,704,369, April 27, 2010

High Temperature Solid Oxide Electrolyzers for Syngas
Haldor-Topsoe

Fuel from Air

Air (401 ppm CO_2)

↓ etherial solvent



↓

Carbamates and Bicarbonates $\xrightarrow[\text{in situ hydrogenation}]{H_2\text{, 50 Bar}}$ $CH_3OH + H_2O$ + free amine

in situ hydrogenation
Homogeneous catalysts
150 - 165 ^{o}C

↑

Distilled Methanol
(63% conversion with 99% selectivity)

Unpublished Results, USC

Solar Thermal Conversions

$$CO_2 + 3\ FeO \longrightarrow CO + Fe_3O_4$$

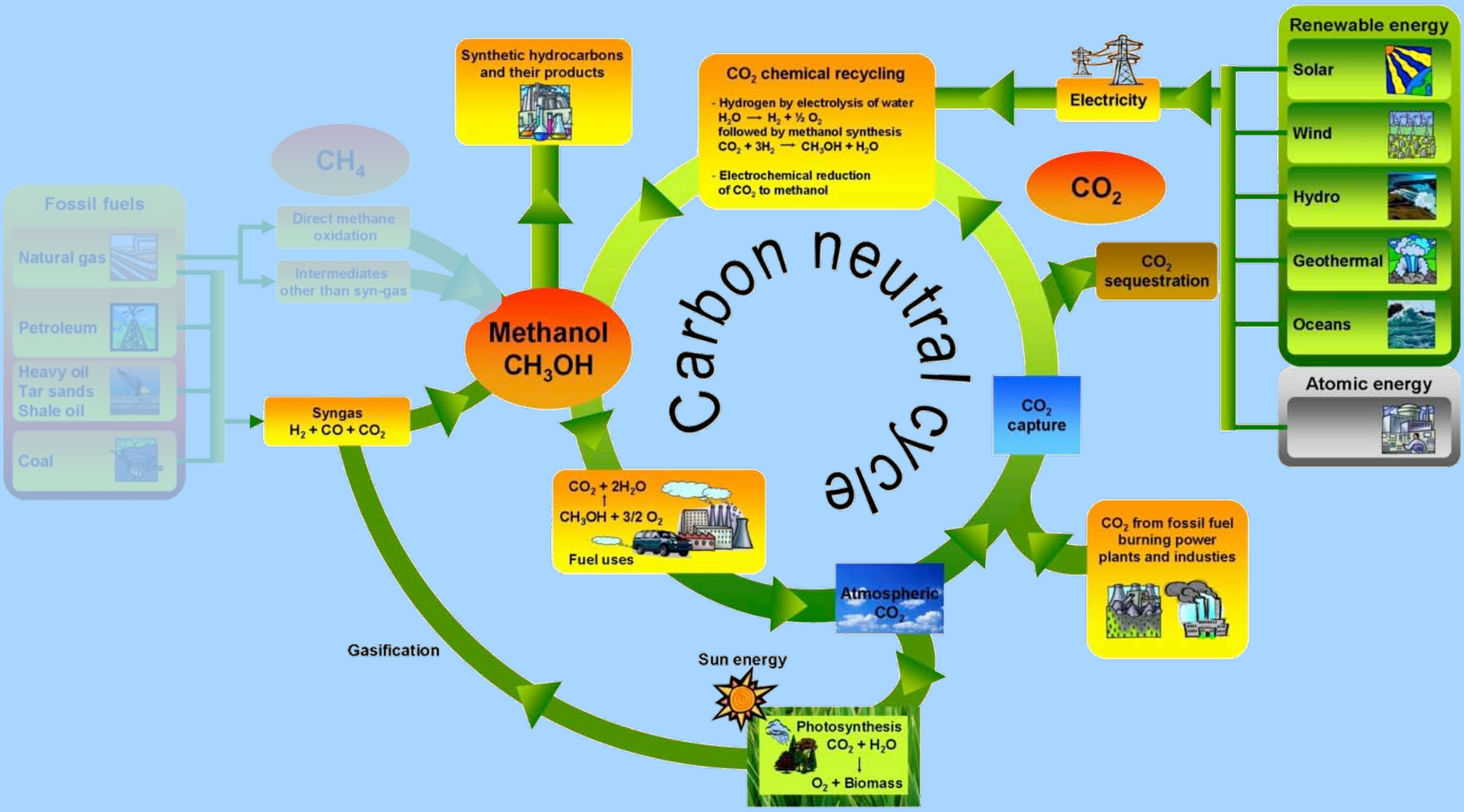
$$Fe_3O_4 \longrightarrow 3\ FeO + 1/2\ O_2$$

Overall

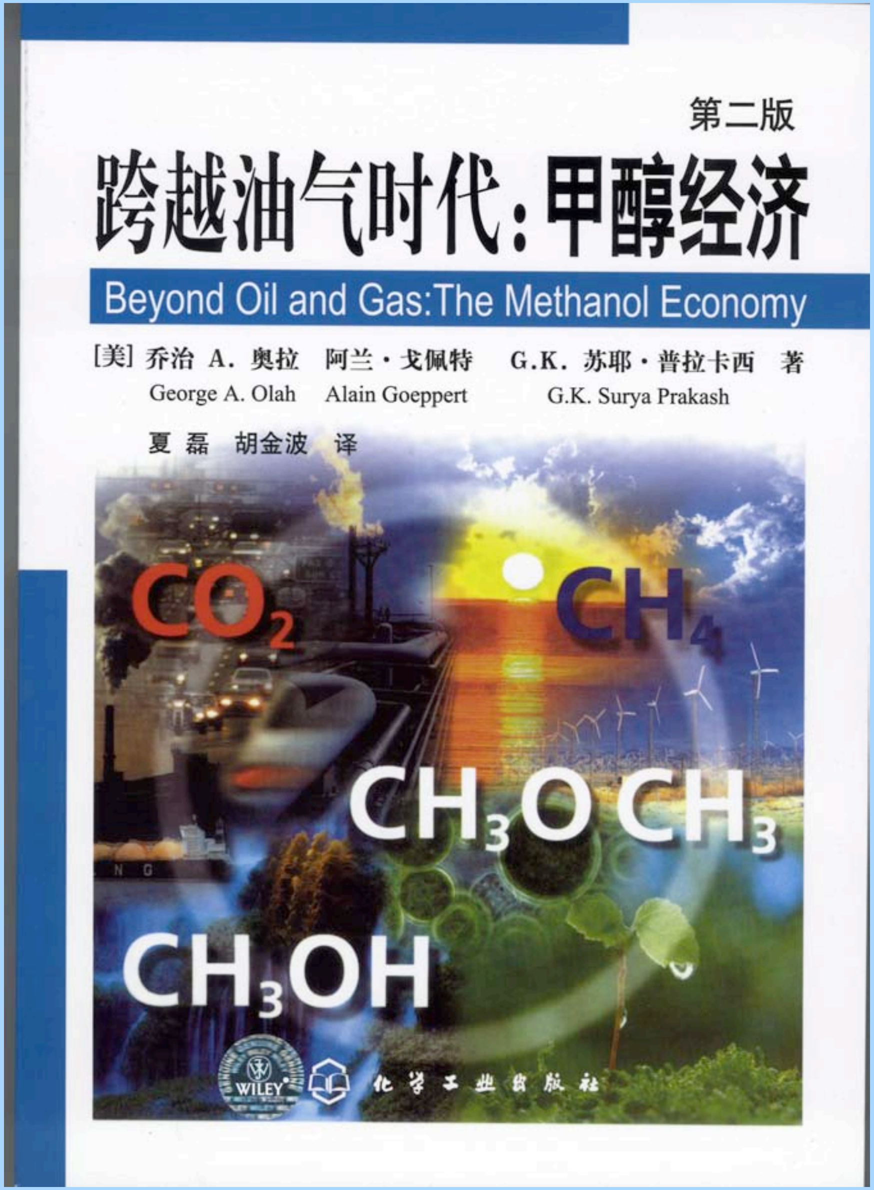
$$CO_2 \longrightarrow CO + 1/2\ O_2$$

Sunshine to Petrol: Sandia National Laboratory Project

The Methanol Economy



Anthropogenic Carbon Cycle


第二版
跨越油气时代:甲醇经济
Beyond Oil and Gas:The Methanol Economy
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George A. Olah Alain Goeppert G.K. Surya Prakash
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CO_2
CH_4
CH_3OCH_3
CH_3OH
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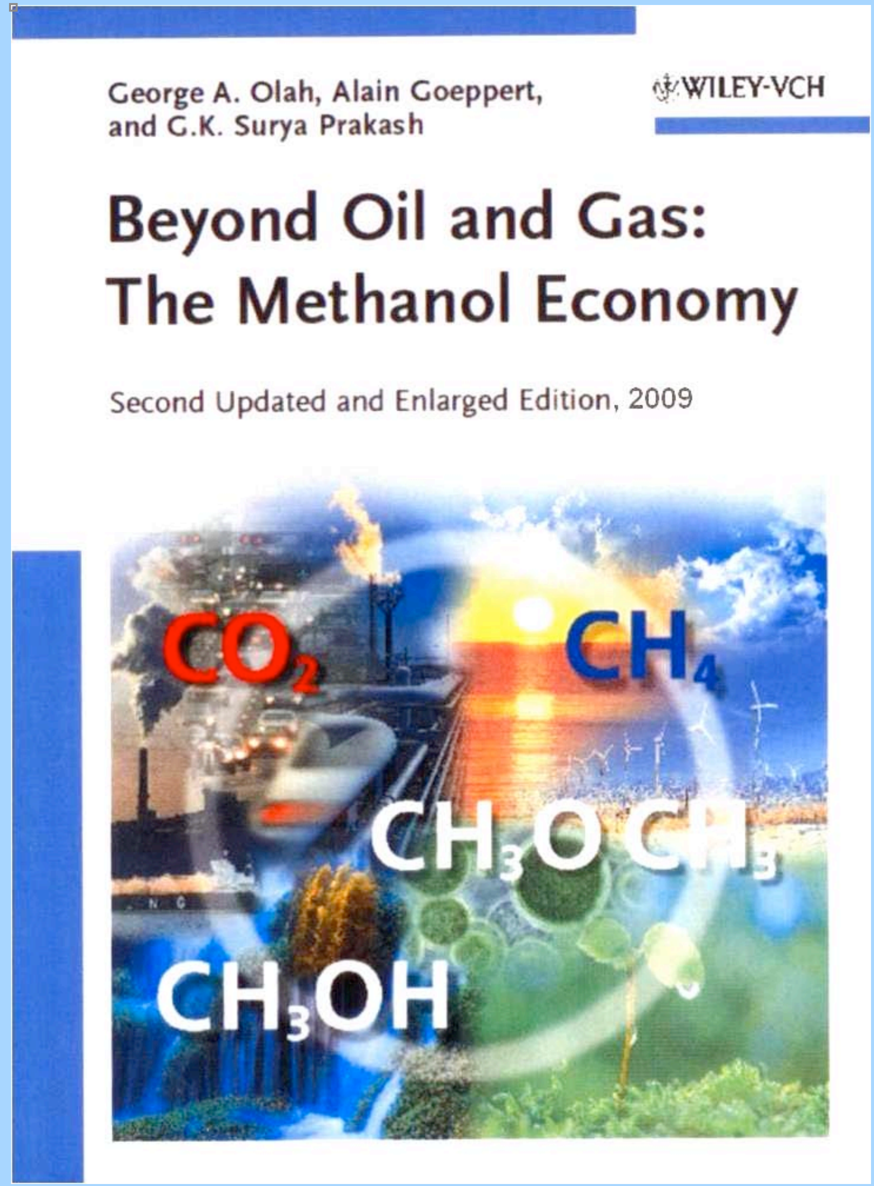
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CO_2
CH_4
CH_3OCH_3
CH_3OH

SUMMARY

Ubiquitous Methanol as a Fuel and Feedstock

Natural (Shale) Gas (higher hydrocarbons)

$\downarrow$

Coal $\longrightarrow$ CH_3OH $\longleftarrow$ Biomass, waste or any carbon source

$\uparrow$

CO_2

Low Hanging Fruit

(KISS Principle: Bridge Fuel in the Short Term and Renewable Carbon Neutral fuel in the Long Term!)

Noblel Laureate, Professor George A. Olah, Main Proponent of the Methanol Economy Concept.