Towards Solar Fuels

Deniz Uner

Chemical Engineering

Middle East Technical University,
ODTU Ankara 06800

Turkey

November 23, 2021

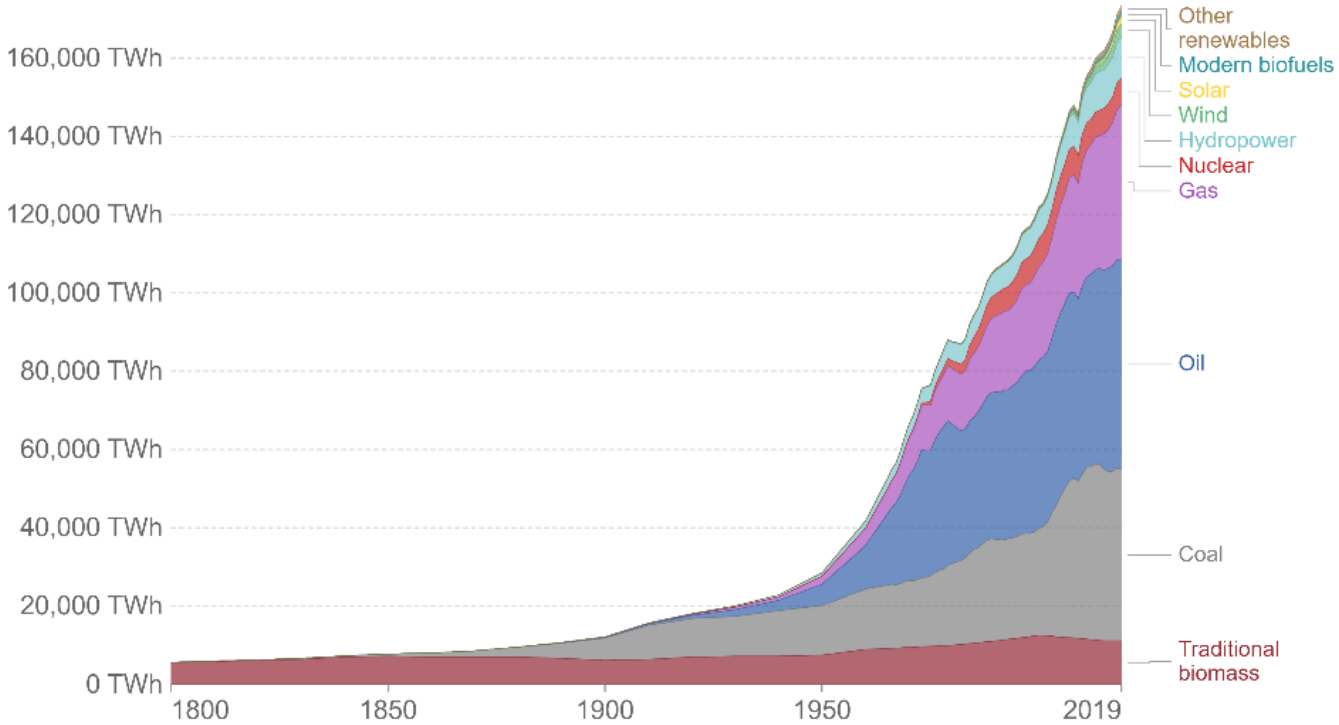
SolarFuels NOW workshop

THE FIRST QUESTION

HOW MUCH ENERGY DO WE SPEND, WHAT IS THE EFFICIENCY?

Global primary energy consumption by source

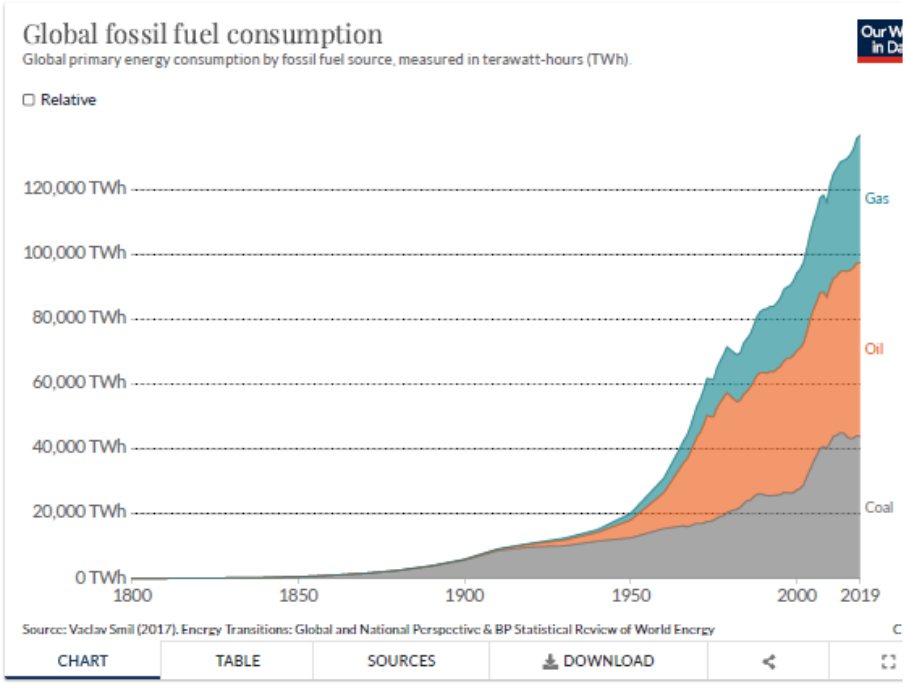
Primary energy is calculated based on the 'substitution method' which takes account of the inefficiencies in fossil fuel production by converting non-fossil energy into the energy inputs required if they had the same conversion losses as fossil fuels.



Source: Vaclav Smil (2017) & BP Statistical Review of World Energy

OurWorldInData.org/energy • CC BY

The annual fossil fuel consumption



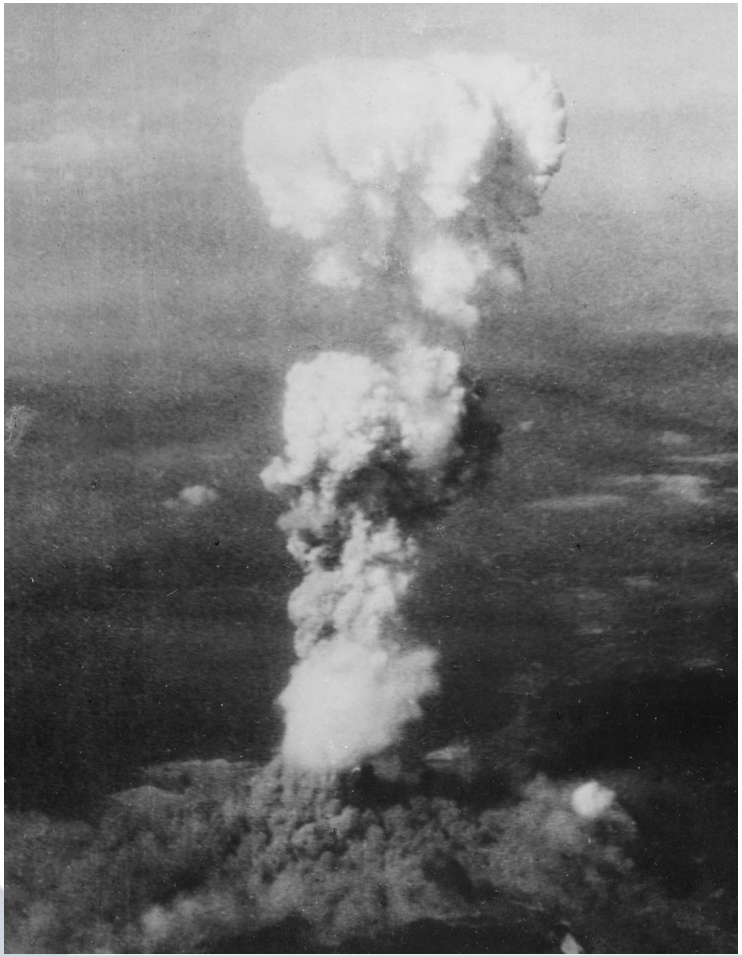
https://ourworldindata.org/fossil-fuels

Annual fosil fuel consumption in 2019

= 136761 TWh= 4.9 10^{20}J

A reference frame for comparison is needed!

Hiroshima Atomic Bomb

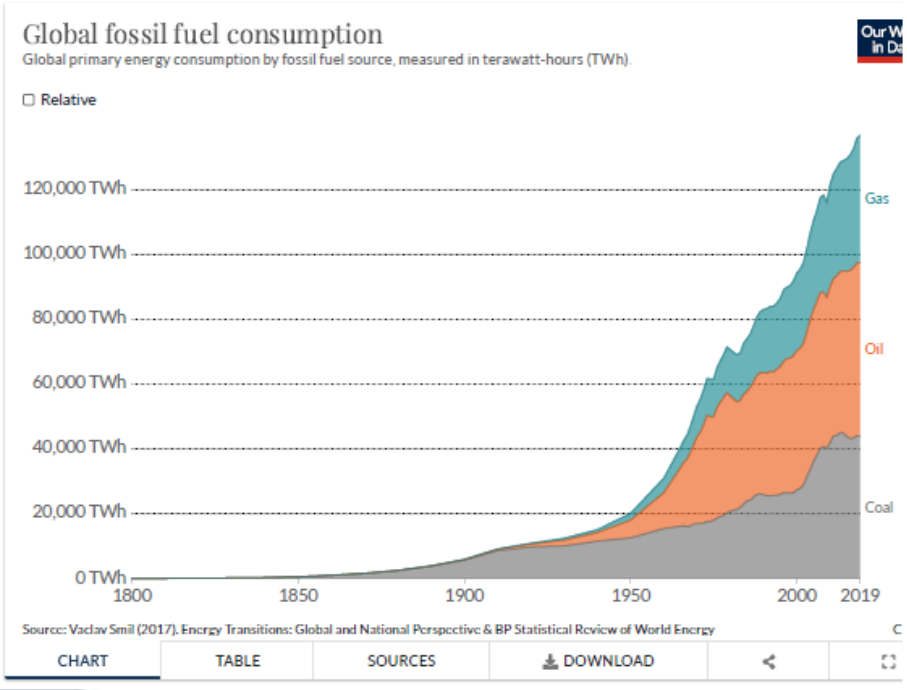


Mushroom has risen 16 km

63 TJ Blast yield= 63 10^{12} J

Revisit the Hiroshima A-bomb with Database: 55-67
http://www.hisof.jp/03database/0106.pdf

Compare with the annual fossil fuel consumption



https://ourworldindata.org/fossil-fuels

Annual fosil fuel consumption in 2019

= 136761 TWh= 4.9 10^{20}J

- Equivalent of 15 Atomic bombs/min
- Where does this energy go?

Energy is a state function

- Initial state: system at a temperature T_0 and E joules of energy is available in the form of heat and/or work.
- Final state: Energy is fully dissipated. What is the temperature?

How much increase in temperature, if all of the energy is dissipated to the atmosphere?

Annual fosil fuel consumption= 136761 TWh,

E=4.9 10^{20}J

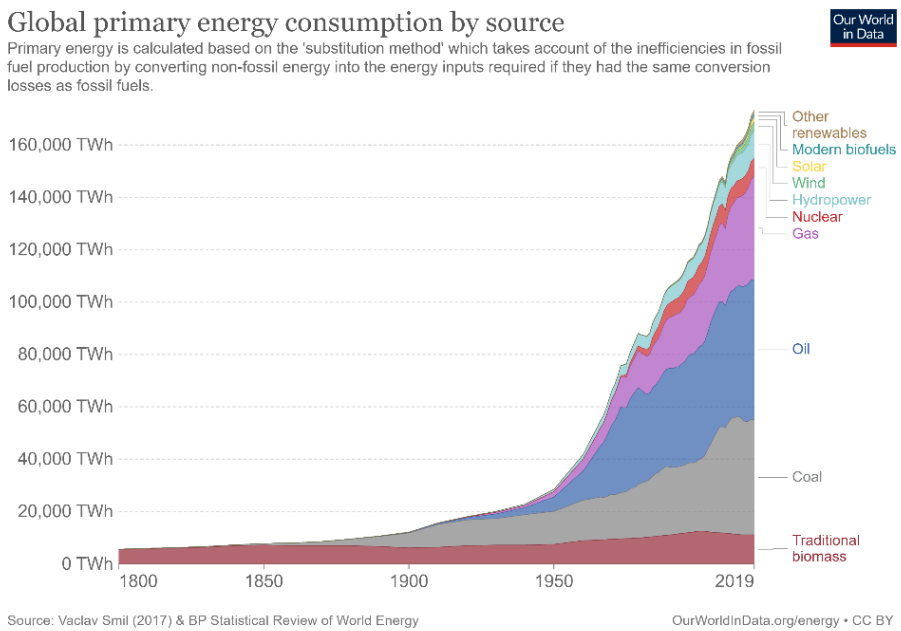
Atmosphere mass = 5.15 10^{18} kg,

Assume Atmosphere as N_2+O_2 $\overline{MW} = 29\frac{g}{gmol}, C_p^* = \frac{7}{2}R$

$\Rightarrow$ ΔT=0.17^{o}C/year

Climate Change: Global Temperature | NOAA Climate.gov Reports a temperature increase of 0.17^{o}C/decade

- 267 Gt ice melting/year, accounts for 0.8 10^{20}J
- Warming up of surface waters and increase in evaporation/condensation rates can account for the rest.



…. Which takes account of the inefficiencies in fossil fuel production by converting non-fossil energy inputs required if they had the same conversion losses as fossil fuels.

A passenger car is ~1000 kg, while the passenger is ~100 kg! 10 % efficiency.

Typical chemical to mechanical energy conversion efficiency is ~10%.

Riding a car is, at best, 1% efficient!

THE NEXT QUESTION

CAN WE SELECTIVELY PRODUCE CONVENTIONAL FUELS FROM METHANE, WATER AND CO_2 ?

Current strategies for synthetic fuels

- Syngas related reactions
  - Using reforming reactions to produce syngas

SMR $\mathrm{CH_4 + H_2O \rightleftharpoons CO + 3H_2}$

DRM $\mathrm{CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2}$

WGS $\mathrm{CO + H_2O \rightleftharpoons CO_2 + H_2}$

  - Syngas to Fischer Tropsch

$$\mathrm{2CO + 2H_2} \rightarrow -CH_2- \ +H_2O \ (or\ CO_2)$$

  - Syngas to Methanol then methanol to olefins

$$\mathrm{CO + 2H_2} \rightarrow CH_3OH \rightarrow -CH_2- \ +H_2O$$

Reforming reactions, what is the bottleneck?

Reactions	$\Delta H^o_{298K}\ (\frac{kJ}{mol})$	$\Delta G^o_{298K}\ (\frac{kJ}{mol})$	$T\ at\ \Delta G = 0$
Steam Methane Reforming			
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	205.9	142.0	891 K
Dry Reforming of Methane			
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	247.0	170.6	915 K
Water-Gas Shift			
$CO + H_2O \rightleftharpoons CO_2 + H_2$	-41.1	-28.6	1093 K
Methane Decomposition			
$CH_4 \rightleftharpoons C + 2H_2$	74.6	50.5	816 K
Boudouard Reaction			
$2CO \rightleftharpoons CO_2 + C$	-172.4	-120.0	975 K
CO_2 and CO Reduction			
$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O$	-90.1	-62.8	902 K
$CO + H_2 \rightleftharpoons C + H_2O$	-131.3	-91.4	947 K

The bottlenecks are……

- At low temperatures, we have thermodynamic limitations of an endothermic reaction.

- The temperatures at which we overcome thermodynamic bottlenecks, transport limitations prevail. Reformer design is for a heat exchanger, not a reactor. There is no need to optimize a catalyst, we must optimize heat transfer.

- We must manage coke buildup.

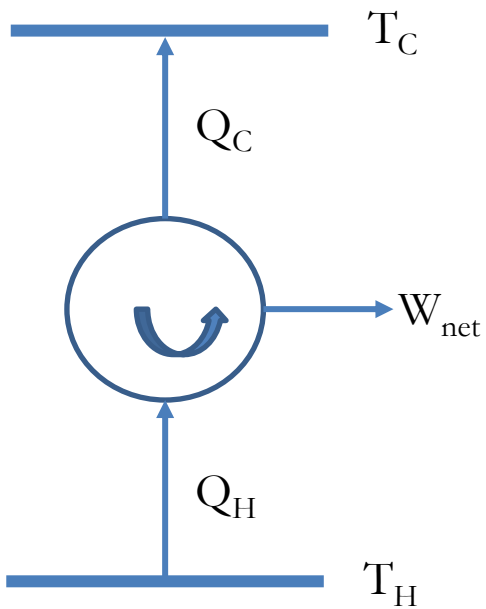
The second law boundaries

- $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$
- ΔH=247.0 kJ/mol ΔG= 170.6 kJ/mol $T(\Delta G=0)$ = 915 K
- We need extra-terrestrial energy input in order not to violate the second law!!!
- In other words,
  - Using any terrestrial thermal energy for the conversion of CO_2 creates more CO_2 than it converts, or else violates the second law!
    - We are bound to use solar energy for CO_2 reduction processes.
      - Direct utilization of solar energy, i.e. artificial photosynthesis
      - Indirect utilization such as photoelectrochemical, PV to chemical
      - Solar thermal energy

Solar Reactors at ODTU

Why CSP can be important?

The Carnot Cycle



$$\eta = -\frac{W_{net}}{Q_H} \times 100$$

For Carnot cycle only

$$\eta = \frac{T_H - T_C}{T_H} \times 100$$

Two reasons:

1. T_H can be very high with CSP
2. CSP can target 100% of solar spectrum.

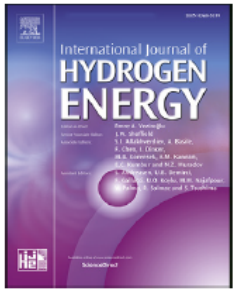
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 44 (2019) 18671–18681

ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Finding the optimum between volatility and cycle temperatures in solar thermochemical hydrogen production: Pb/PbO pair

Atalay Calisan, C. Guvenc Ogulgonen, Serkan Kincal, Deniz Uner*

Department of Chemical Engineering, Middle East Technical University, 06800, Ankara, Turkey

ARTICLE INFO

Article history:
Received 26 August 2018
Received in revised form
13 November 2018

ABSTRACT

A pilot unit for a concentrated solar thermal reactor with solar tracking was constructed. A 70 cm diameter concentrator dish could provide temperatures around 800 °C at a fairly steady rate. In the search for a redox pair that can work at such temperatures, studies were conducted on the feasibility of the Pb/PbO cycle for the splitting of H_2O for H_2 production.

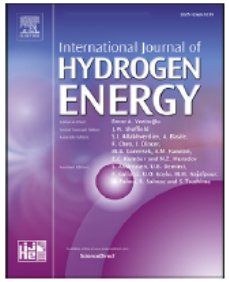
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 44 (2019) 18682–18693

ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Steam methane reforming over structured reactors under concentrated solar irradiation

Check for updates

*Atalay Calisan, C. Guvenc Ogulgonen, Arda Yilmaz, Deniz Uner, Serkan Kincal**

Department of Chemical Engineering, Middle East Technical University, 06800, Ankara, Turkey

ARTICLE INFO

Article history:
Received 27 August 2018
Received in revised form
31 March 2019
Accepted 4 April 2019
Available online 10 May 2019

ABSTRACT

Intermittent nature of solar energy and solution strategies for steam methane reforming reaction powered by concentrated solar energy over Ni/mullite and Pd/CeO_2/mullite catalysts were demonstrated. The solar concentration was achieved using a parabolic mirror with a 70 cm, delivering concentrated solar flux onto a focal area that is approximately 3 cm in diameter. The solar field tests conducted on monolithic catalyst support structures were compared with the laboratory scale measurements on powdered catalysts. Despite the fluctuations in solar irradiation, CH_4 conversions higher than 90% could be obtained.

THE NEXT QUESTION

CAN WE MIMIC NATURE TO PRODUCE CHEMICALS FROM SUN WATER AND CO_2 ?

CO_2 mitigation the ultimate dream

- $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

If not,

- $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

Thermodynamics

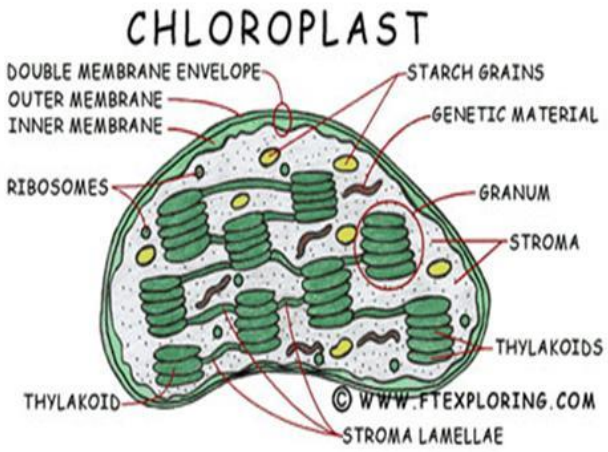
Reaction	ΔG_f (kJ/mol HC product)	ΔG_f (kJ/mol O_2)
$CO_2 + 2H_2O \Rightarrow CH_4 + 2\ O_2$	801.0	400.5
$CO_2 + 2H_2O \Rightarrow CH_3OH + 1½\ O_2$	689.2	459.5
$2\ CO_2 + 3H_2O \Rightarrow C_2H_5OH + 3\ O_2$	1306.6	435.5
$H_2O + CO_2 \Rightarrow 1/6\ C_6H_{12}O_6 + O_2$	2880.0	480.0
$H_2O \Rightarrow H_2 + ½\ O_2$	228.6	457.2

Thermodynamically the most demanding reaction is water splitting!

Learning from nature-
Confinement in space for better selectivity

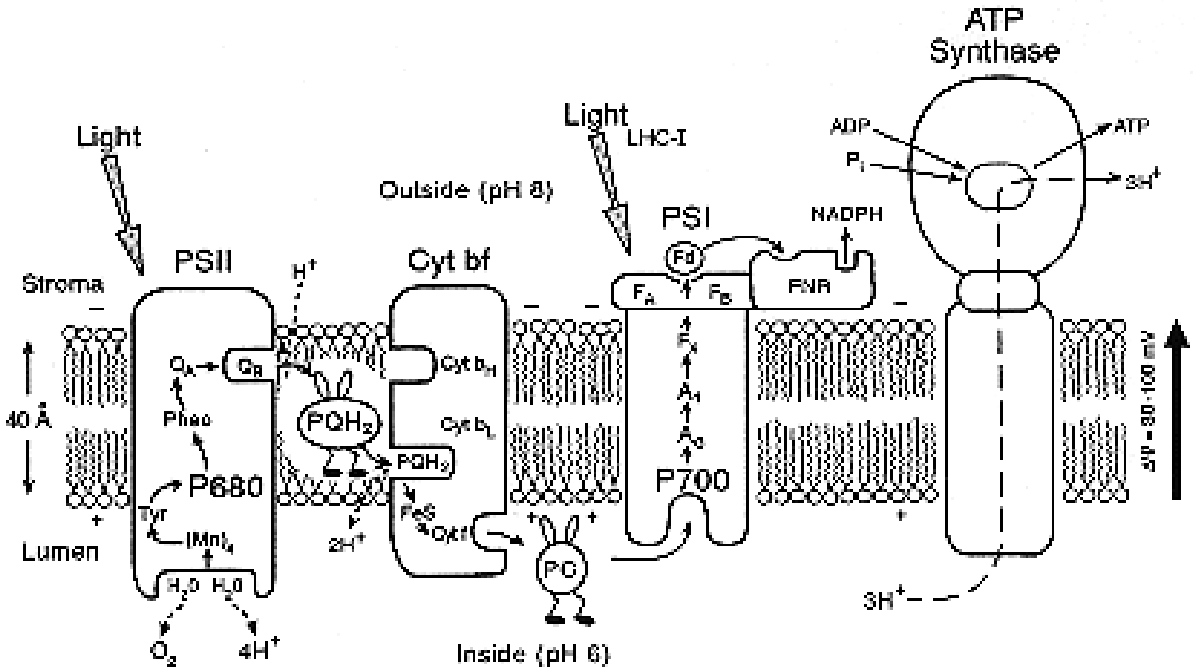
Photosynthesis is an excellent example of confinement in space.

- Oxidation processes take place using illumination in thylakoids
- Reduction processes take place in dark in stroma
- Proton and electron transport



The problem to solve is oxygen!

The natural factory

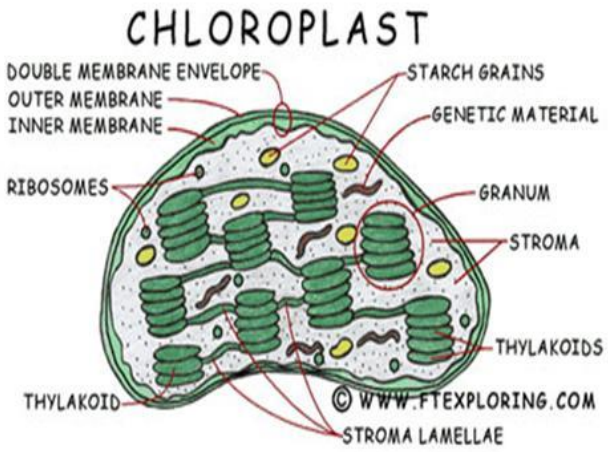


WG: Whitmarsh and Govindjee in Concepts in Photobiology: Photosynthesis and Photomorphogenesis, New Delhi; and Kluwer Academic/Dordrecht, pp. 11-51

Confinement in space

Artificial photosynhtesis

$CO_2 + H_2O \rightarrow CH_4$ + (oxygen)

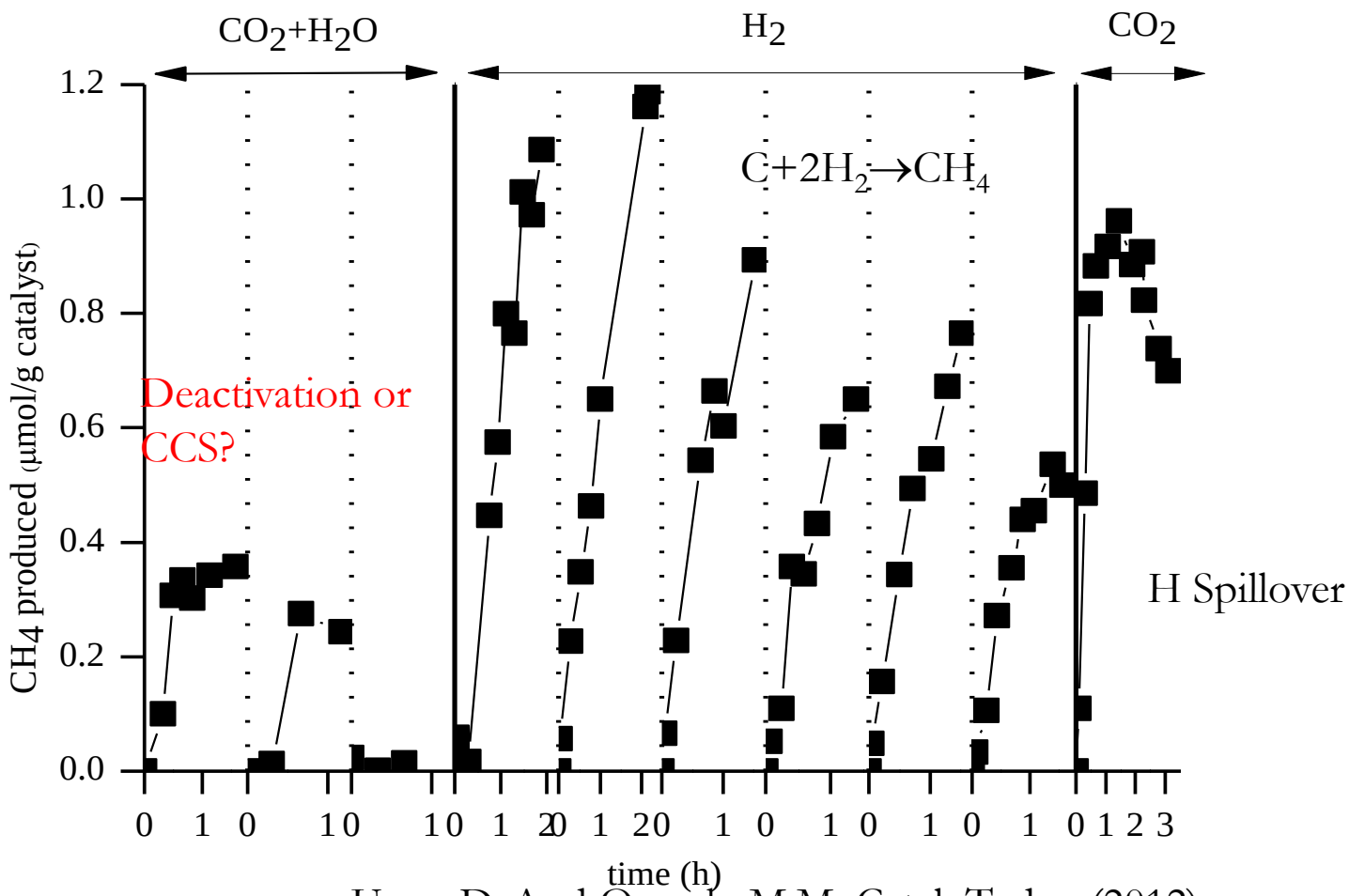


Ozcan, Yukruk, Akkaya, Uner, Appl. Catal. B.-Environ. 71 (2007) 291-297

Uner. D, Oymak, M.M., Ipek, B. Int. J. Global Warming 3 (2011) 142

Uner, D; Oymak, MM Catalysis Today, 181 (2012) 82-88.

Pt/TiO_2 under UV irradiation



Uner, D. And Oymak, M.M. Catal. Today, (2012)

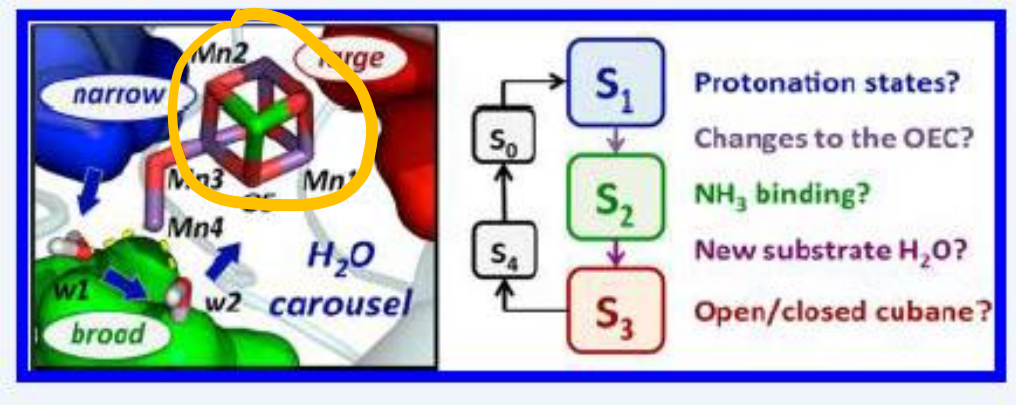
Nature's mystery has yet to be solved!

? → O_2 @ 198 K

Single site catalysts confine events in space:

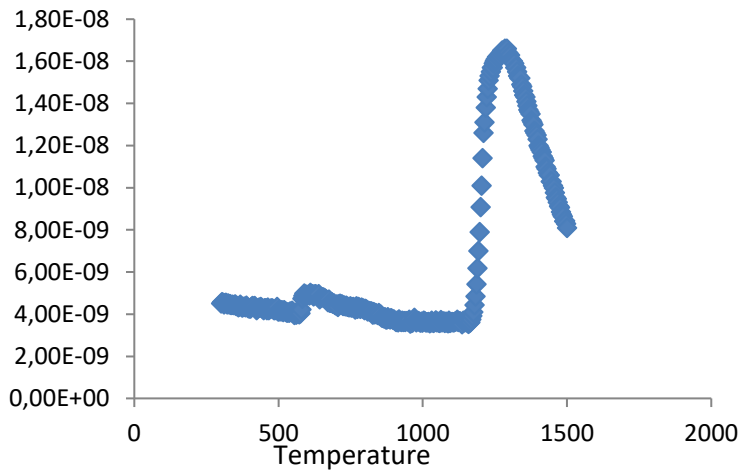
Oxygen evolving complex in photoynthetic plant cells

Oxygen evolution is the most energy demanding process

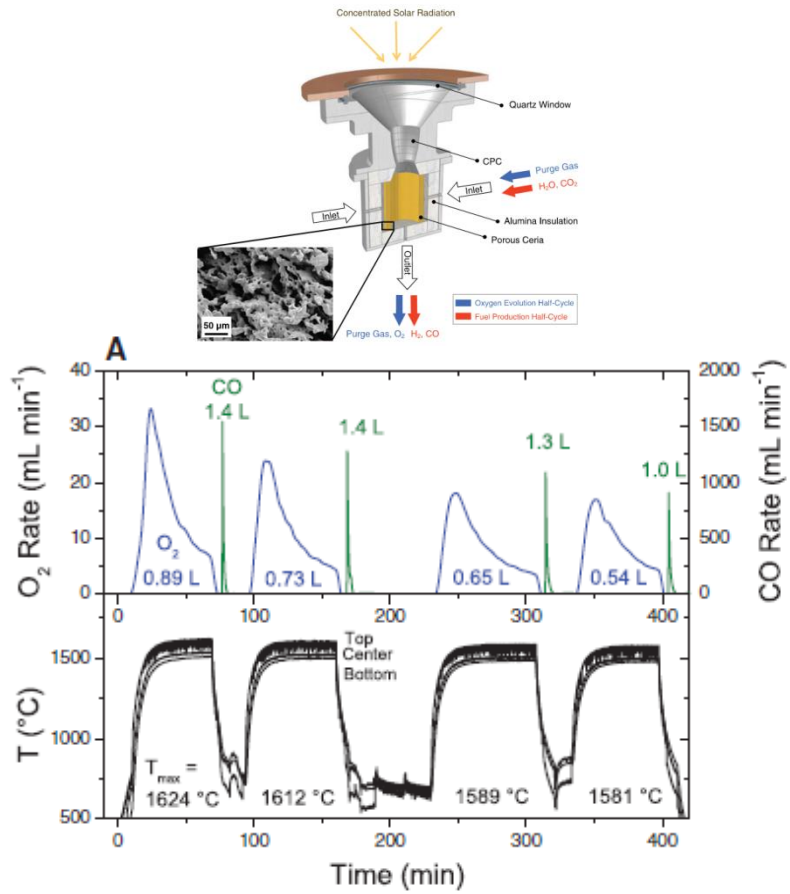


Askerka, Brudwig and Batista,Acc. Chem. Res, 50(2017)41-48

CONCENTRATED SOLAR ENERGY



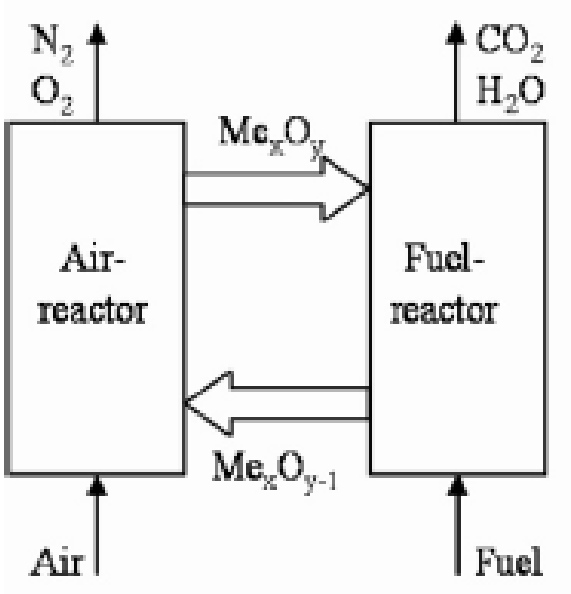
N Can Aksu MS Thesis 2012



Chueh et al. Science, 2010

Level 1: Chemical looping

- Proposed as an alternative for oxy fuel combustion systems.
- A metal oxide shuttles oxygen between a dual reactor system.



Markstrom et al. CES (2010)
Çalışan A. MS Thesis
Kanca, A. PhD Thesis

Chemical looping in (Solar) thermochemical redox cycles

Water Cycle

Higher temperature T_H

$MO_x \rightarrow MO_{x-2} + 1/2\ O_2(g)$

Lower temperature T_L

$2H_2O(g) + MO_{x-2} \rightarrow MO_2 + 2\ H_2(g)$

The net reaction

$2\ H_2O(g) \rightarrow O_2 + 2\ H_2(g)$

CO_2 cycle

Higher temperature T_H

$MO_x \rightarrow MO_{x-2} + 1/2\ O_2(g)$

Lower temperature T_L

$2CO_2(g) + MO_{x-2} \rightarrow MO_2 + 2\ CO\ (g)$

The net reaction

$2\ CO_2(g) \rightarrow O_2 + 2\ CO\ (g)$

FISCHER TROPSCH TECHNOLOGGY

Anything to liquids (XTL)

coal (CTL)

natural gas (GTL)

biomass (BTL)

SYNGAS, CO + H_2 is produced by gasification and/or reforming of the feedstocks. SYNGAS is converted to hydrocarbons over a chain length distirbution over Fe or Co catalysts.

$$\text{FTS}: \quad CO + 2H_2 \rightarrow -CH_2- + H_2O \quad -165\,\text{kJ mol}^{-1} \quad [1]$$

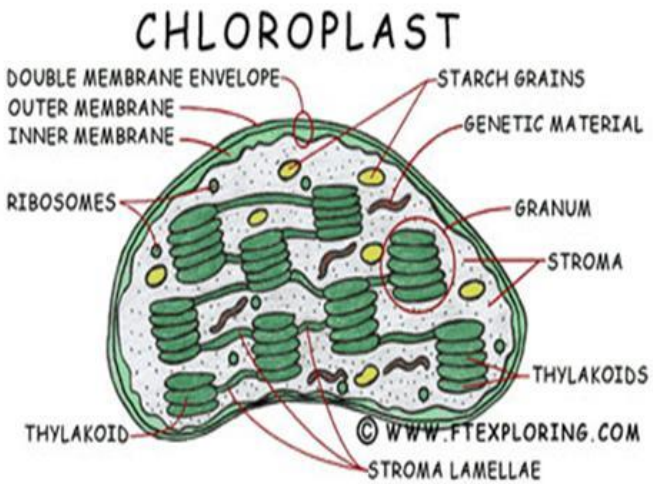
$$\text{WGS}: \quad CO + H_2O \rightleftharpoons H_2 + CO_2 \quad -42\,\text{kJ mol}^{-1} \quad [2]$$

Figure 5 Photo of the Sasol-QP Oryx GTL plant in Qatar, showing the air separation units (ASUs), the auto-thermal reformers (ATRs), and the Fischer–Tropsch synthesis (FTS) slurry reactors. The product work-up section located behind the FTS reactors is not visible (photo courtesy of Sasol).

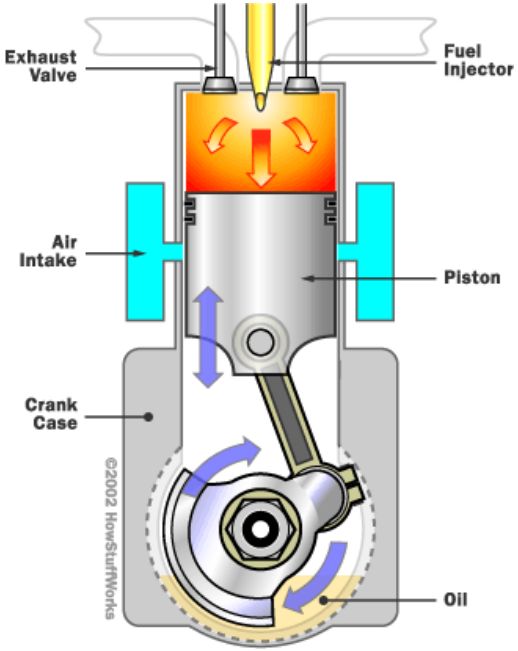
vandeLoostrecct et al. in Comprehensive Inorganic Chemistry, Elsevier 2013 p 525-557

From sun to combustion chamber?

The plant cell



The Two Stroke Diesel Engine



Time to reconsider how efficient we live!