Chemical energy storage - and how we can exploit it to improve energy conversion processes

Ian S. Metcalfe
School of Engineering
Newcastle University

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A short history of fossil fuels for chemical energy storage

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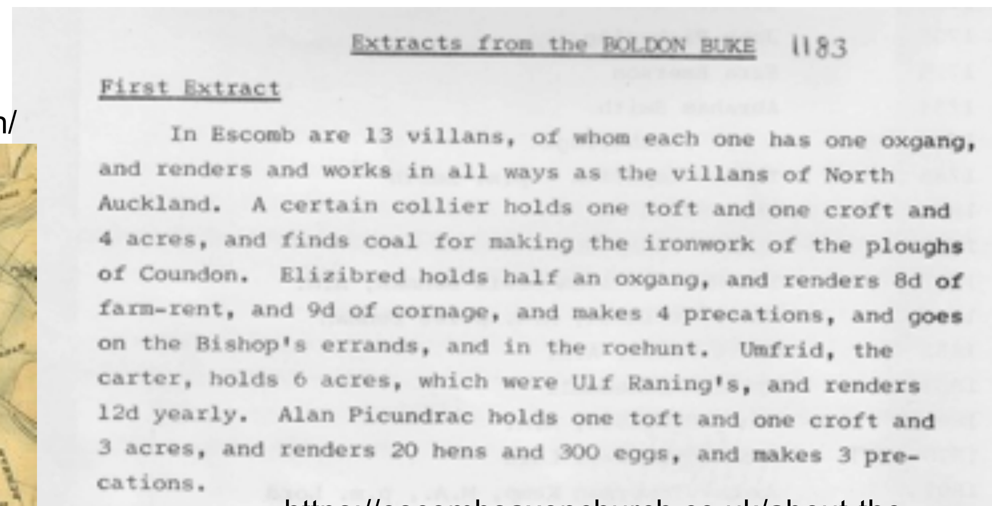
- ➢**Newcastle**
- ➢**The 'New Castle' was built in 1080**
- ➢**Boldon Book (1183, similar to the Domesday book but commissioned by the Bishop of Durham) mentions a collier – North of England**

https://mininginstitute.org.uk/education/



Extracts from the BOLDON BUKE 1183

First Extract

In Escomb are 13 villans, of whom each one has one oxgang, and renders and works in all ways as the villans of North Auckland. A certain collier holds one toft and one croft and 4 acres, and finds coal for making the ironwork of the ploughs of Coundon. Elizibred holds half an oxgang, and renders 8d of farm-rent, and 9d of cornage, and makes 4 precations, and goes on the Bishop's errands, and in the roehunt. Umfrid, the carter, holds 6 acres, which were Ulf Raning's, and renders 12d yearly. Alan Picundrac holds one toft and one croft and 3 acres, and renders 20 hens and 300 eggs, and makes 3 precations.

https://escombsaxonchurch.co.uk/about-the-church/history/escomb-in-the-bolden-book/

https://mininginstitute.org.uk/education/archive-teaching-uni

general-maps-of-the-coalfield/bells-plans-of-the-northumber

and-durham-coalfield/bell-auckland-coal-district

A short history of fossil fuel chemical energy storage

- Newcastle
- The 'New Castle' was built in 1080
- Boldon Book (1183, similar to the Domesday book but commissioned by the Bishop of Durham) mentions a coalminer – North of England
- 1305 – Newcastle coal was being shipped to London
- 1372 – Newcastle had 2,637 tax payers (coal mining on the Town Moor)
- 1378 – By 1378 Newcastle shipped 15,000 tons of coal per year including exports to Europe

Energy storage and chemical energy storage?

➢**Wikipedia: ‘Energy storage is the capture of energy produced at one time for use at a later time’**

Energy storage and chemical energy storage?

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‘In 1870 Armstrong installed a Siemens dynamo in what was the world's first hydroelectric power station’
https://en.wikipedia.org/wiki/Cragside

Introduction

- ➢Chemical energy storage is a vast topic (not going to talk about batteries)
- ➢What makes a good chemical energy store
- ➢Could we ever have ‘clean’ hydrocarbon fuels?
- ➢Suggest a way to operate a hydrocarbon fuel with a massive reduction in CO_2 emissions and a big improvement in engine efficiency

Objective of this talk

- A chemical energy transformation is never 100% efficient – need to think about what to do about the inefficiencies and waste heat – whole system approach – simple view of e.g. energy densities is not sufficient
- Need a grasp of fundamental (but simple) thermodynamics
- Also simple process flowsheets including opportunities for heat transfer (awareness of how to match e.g. hot and cold streams)
- Don't think of hydrocarbons as dirty – it is the way we use them

Chemical energy storage

- ➢Capacity of carrier (gravimetric and volumetric)
- ➢Lifetime/stability of carrier
- ➢Rate of energy carrier production (T and P)
- ➢Rate of fuel release/carrier destruction (T and P)

Further considerations

- ➢Thermodyamics of production (exothermic versus endothermic)
- ➢Purity issues
- ➢Toxicity of carrier
- ➢State and conditions of carrier
- ➢Thermodyanmics of release (exothermic versus endothermic)
- ➢Use (or not) of existing fuel distribution infrastructure and/or technology
- ➢And finally – reversibility (efficiency) of overall process

Energy density or capacity

- 1 mole water has a mass of 18 g
- 1 litre water is 1 kg or 55 moles

- Gravitational – 1 kg x 10 m x 9.81 m/s2 = 100 J
- Thermal = 4.18 J/g/K x 1000 g x 75 K = 300 000 J
- Phase change = 2 000 J/g x 1000 g = 2 000 000 J
- Chemical = 250 000 J/mol x 55 mol = 13 750 000 J

- Battery = 200 Wh/kg x 1 kg = 720 000 J

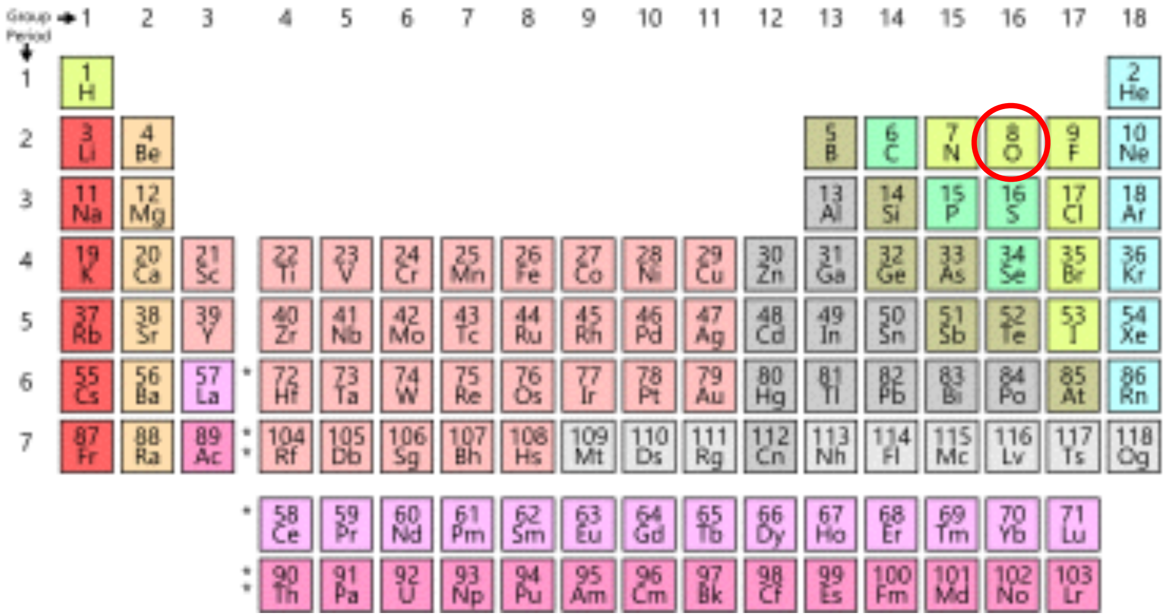
Energy density or capacity

- House – background 600 W so 600 J/s
- 10 p/kWh is 10 p for 3 600 000 J
- 100 minutes costs 10 p

- Gravitational – Fraction of a second
- Thermal = 10 minutes
- Phase change = 1 hour
- Chemical = 7 hours

- Why? Thermal vibrates bonds, chemical breaks bonds

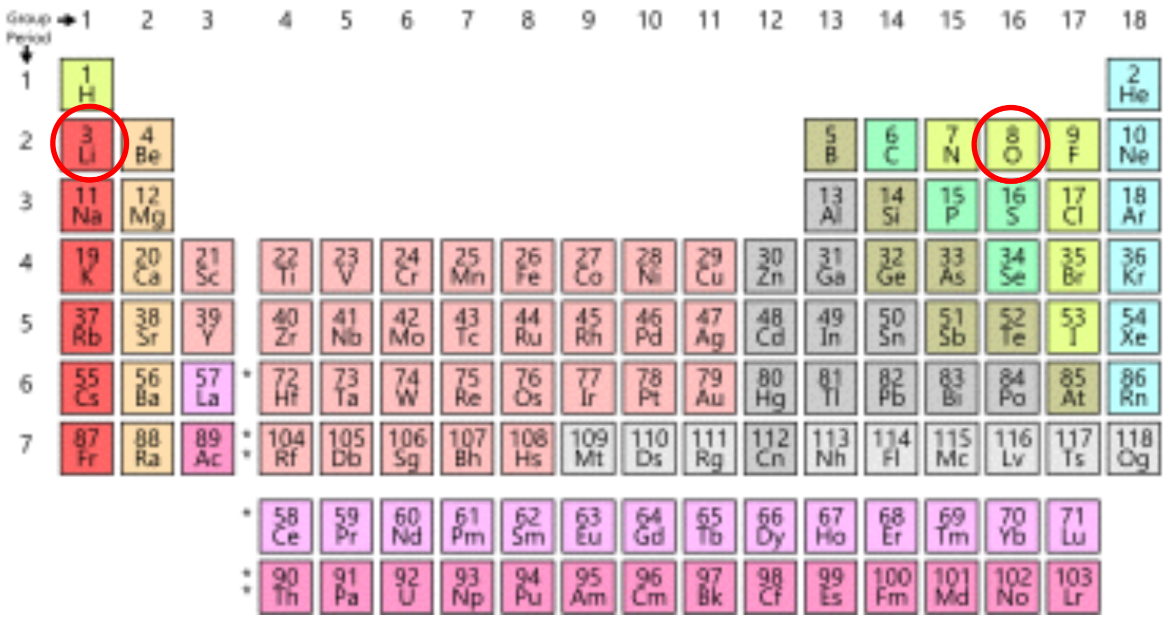
How can we store chemical energy?



https://en.wikipedia.org/wiki/Periodic_table

Readily available oxidant is oxygen

How can we store chemical energy?



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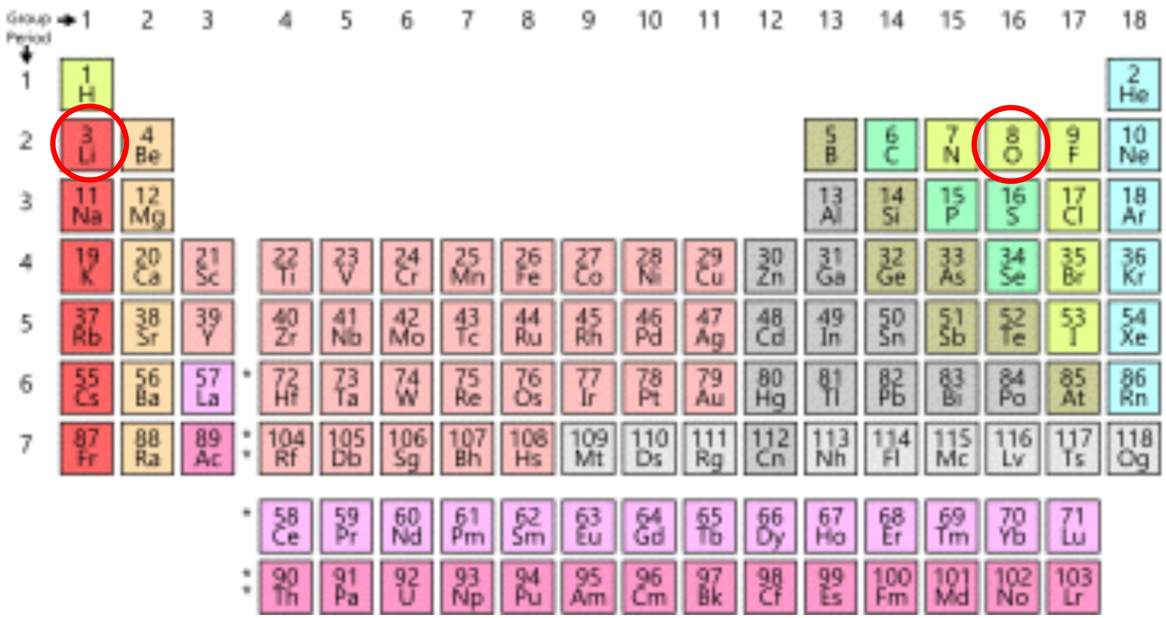
Large heats of reaction per unit mass, e.g., $2Li + O = Li_2O$. Ionic solids.

How can we store chemical energy?



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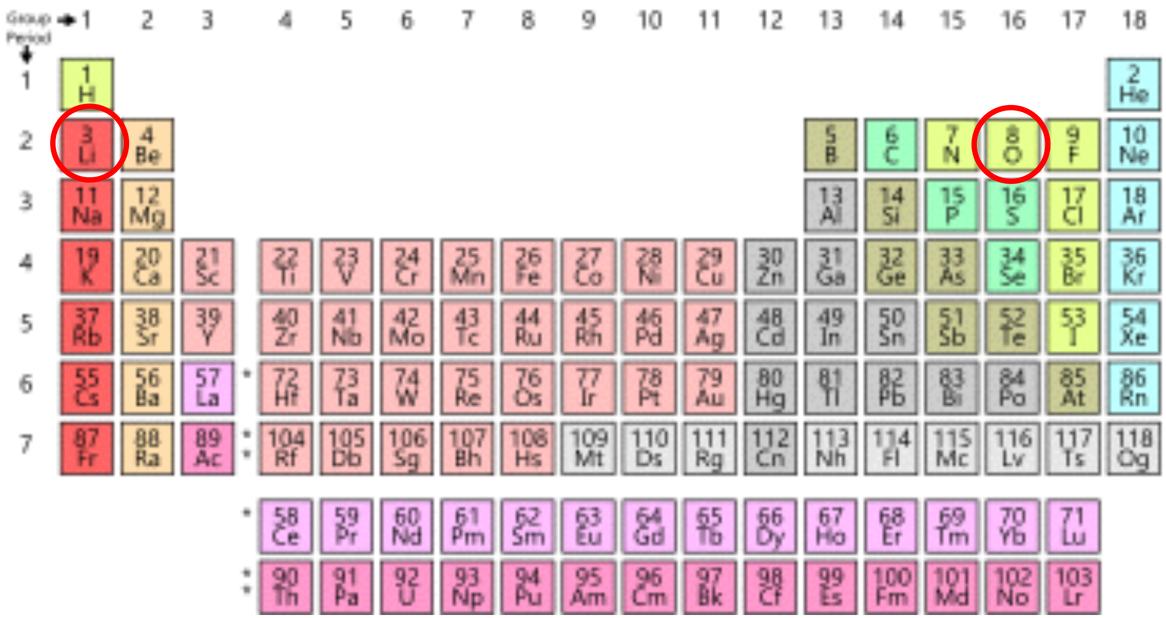
Reduction of Li_2O to Li again (charging the chemical energy store). How can we do that? Need something that will break Li_2O bonds – not easy – do it electrochemically

How can we store chemical energy?



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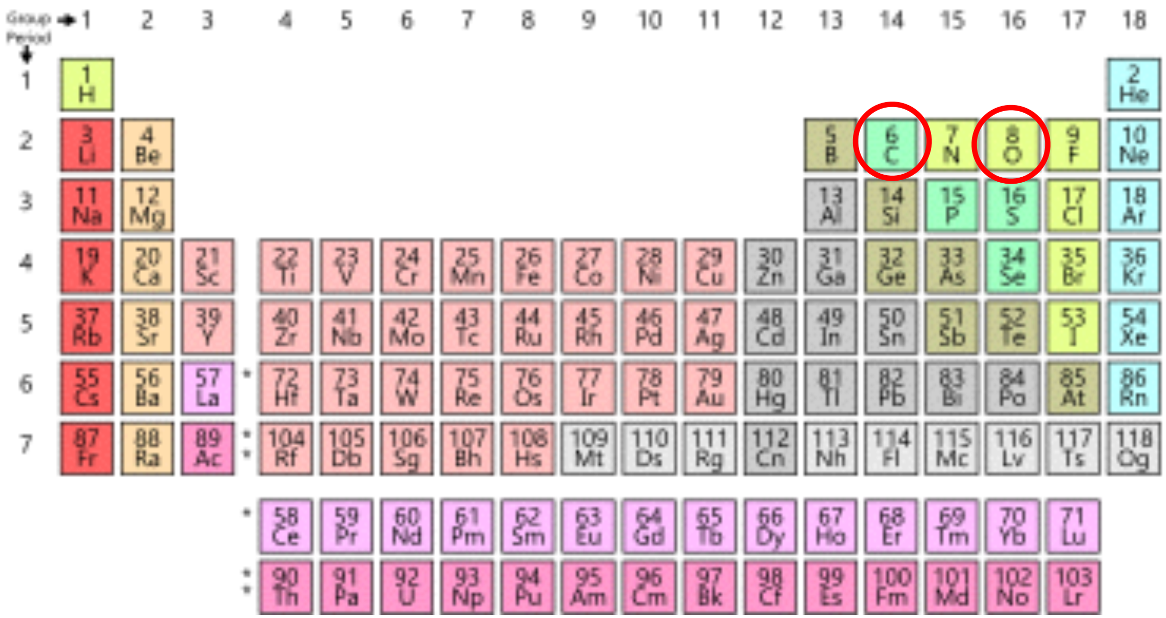
I will not talk about batteries here

How can we store chemical energy?



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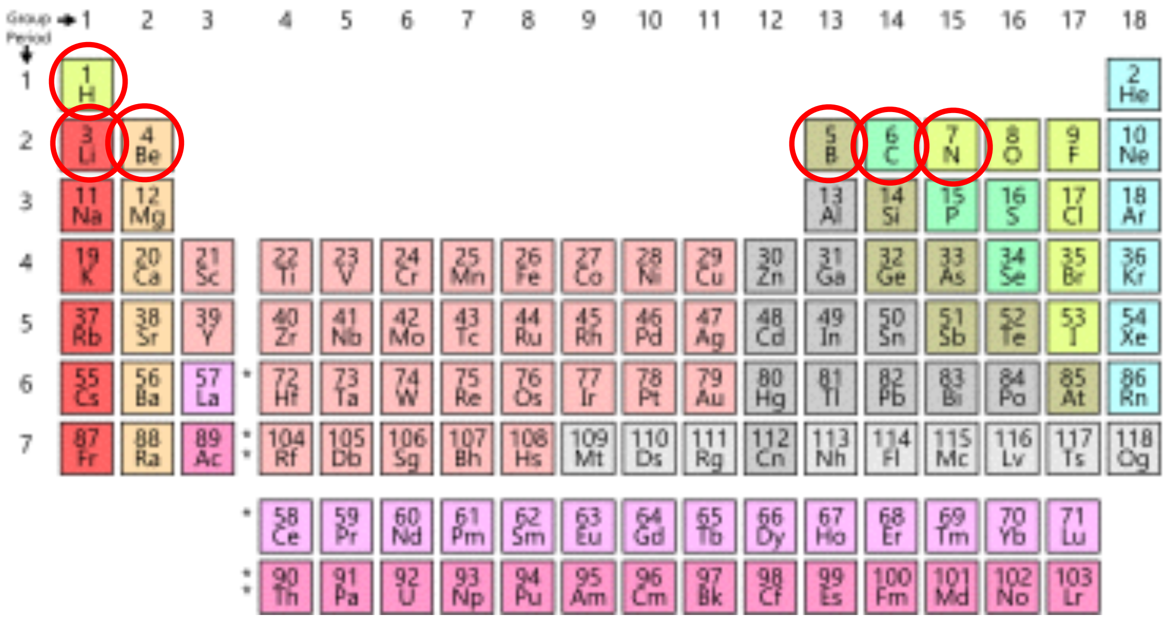
Another solid store used throughout history.

How can we store chemical energy?



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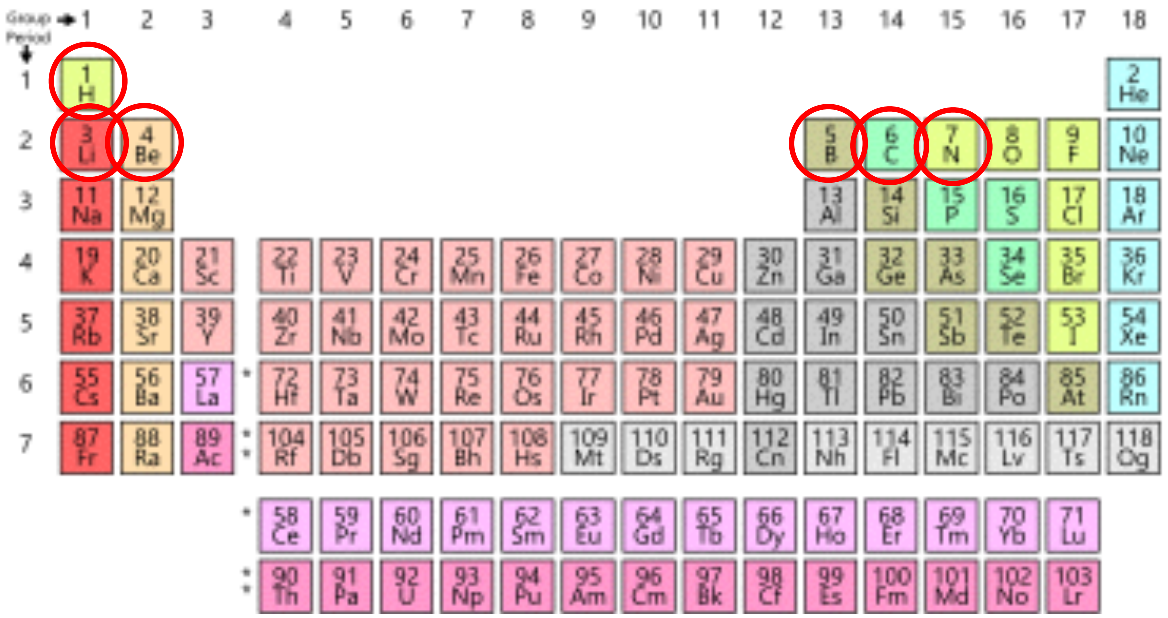
Combination of light elements as chemical energy stores?

How can we store chemical energy?



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H_2, $LiBH_4$, NH_3, hydrocarbons (can be liquids at NTP)

Fuels

Fuel	MJ/kg	MJ/litre	kJ/mol CO2
CH4*	55.5	0.04/24.0	890
CH3OH	19.9	15.8	638
C2H5OH	26.8	21.2	618
Gasoline	46.8	34.1	~600
Carbon	27	21	<600
H2**	142	1.73	infinite

***CH_4 - STP, LNG; **H_2 at 150 bars**

Distribution – CH_4 and organic liquids

H_2 – difficult to transport and store (will return to hydrogen)

Brief history of petroleum

280 to 345 million years ago – Carboniferous period; fossil fuel formation begins.

70,000 years ago – Prehistoric people discover that oil burns with a bright, steady flame.

6th century BCE – Persians discover that a thinner form of bitumen could create flaming missiles.

2,000 years ago – The Chinese begin to drill wells in Sichuan.

1847 – The world's first oil well is drilled in Baku on the Caspian Sea.

1853 – Polish chemist Ignancy Lukasiewicz discovers how to distil oil.

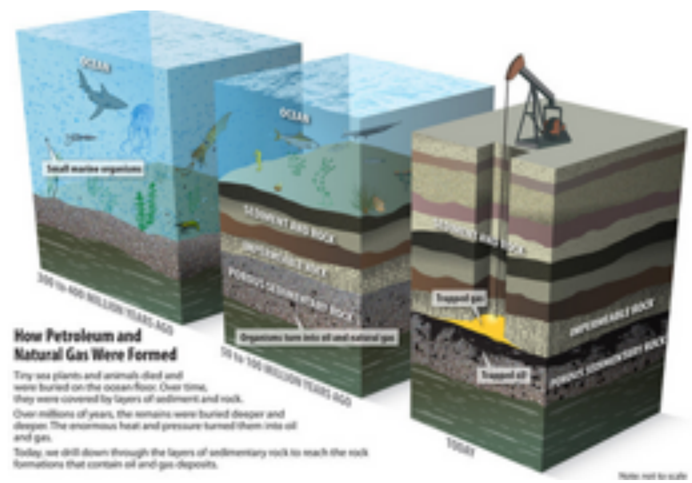
1859 – Edwin L. Drake drills down 70 feet (21meters) in Titus, Pennsylvania, and struck oil to create the US' first oil well.

http://energy4me.org/all-about-energy/what-is-energy/energy-sources/petroleum/

Fossil fuels

➢**Extremely low rate of production - photosynthesis, conversion to liquid and gaseous hydrocarbons over geological time scales**

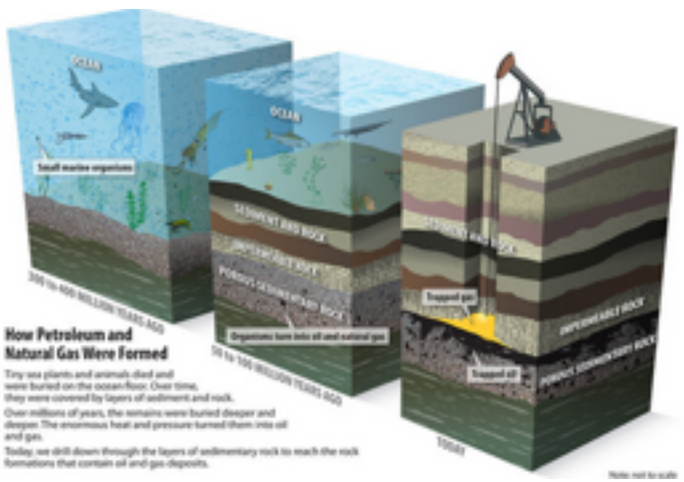
➢**Fossil fuels – we are not capturing energy fast enough anymore!**



https://www.croftsystems.net/oil-gas-blog/what-is-oil-made-of

Fossil fuels

- ➢Combusted to produce CO_2 and H_2O.
- ➢Why don’t we capture the CO_2 to make ‘artificial’ hydrocarbon fuels? Hot research area!
- ➢Case study of hydrogenation of carbon dioxide - CCU



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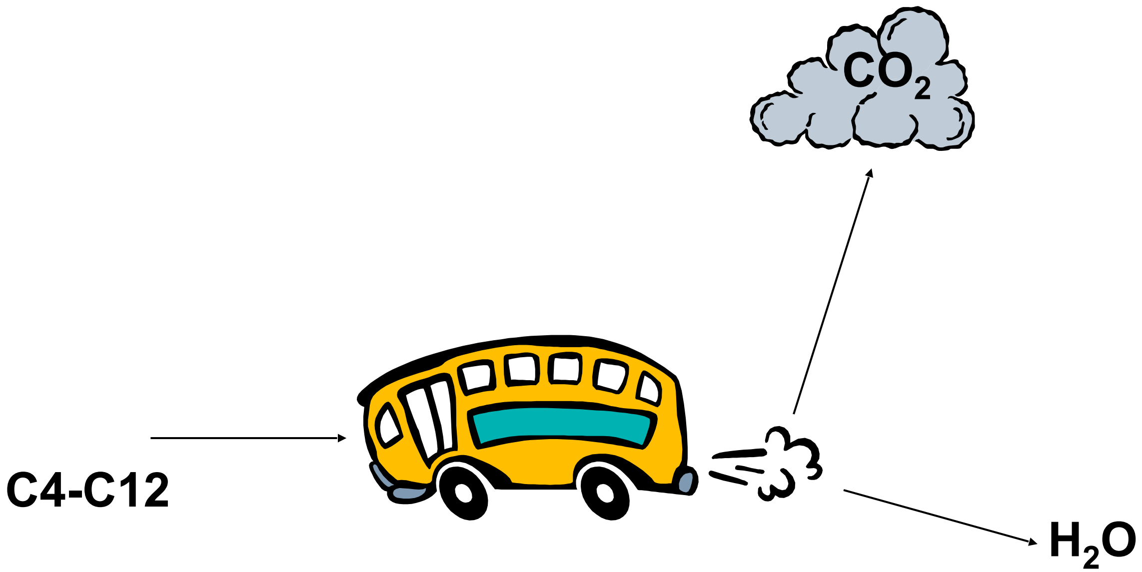
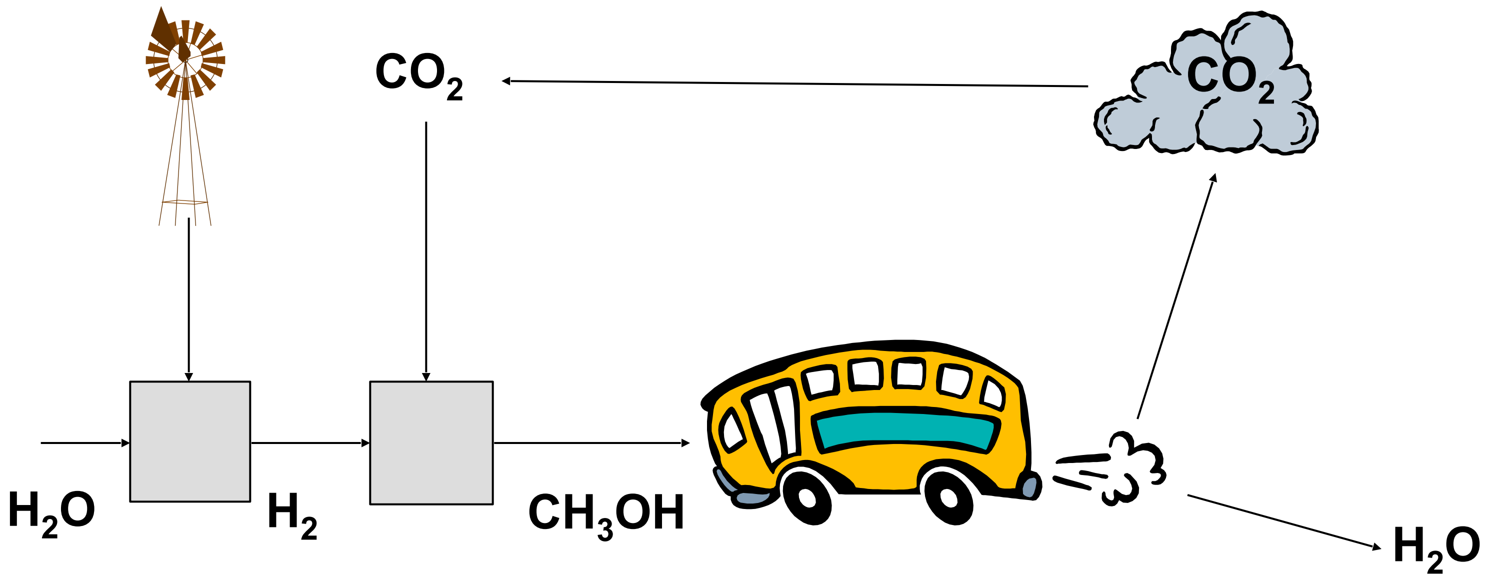
Fossil fuel combustion



Methanol production from CO_2

Methanol production using open carbon cycle:

Does it make sense?



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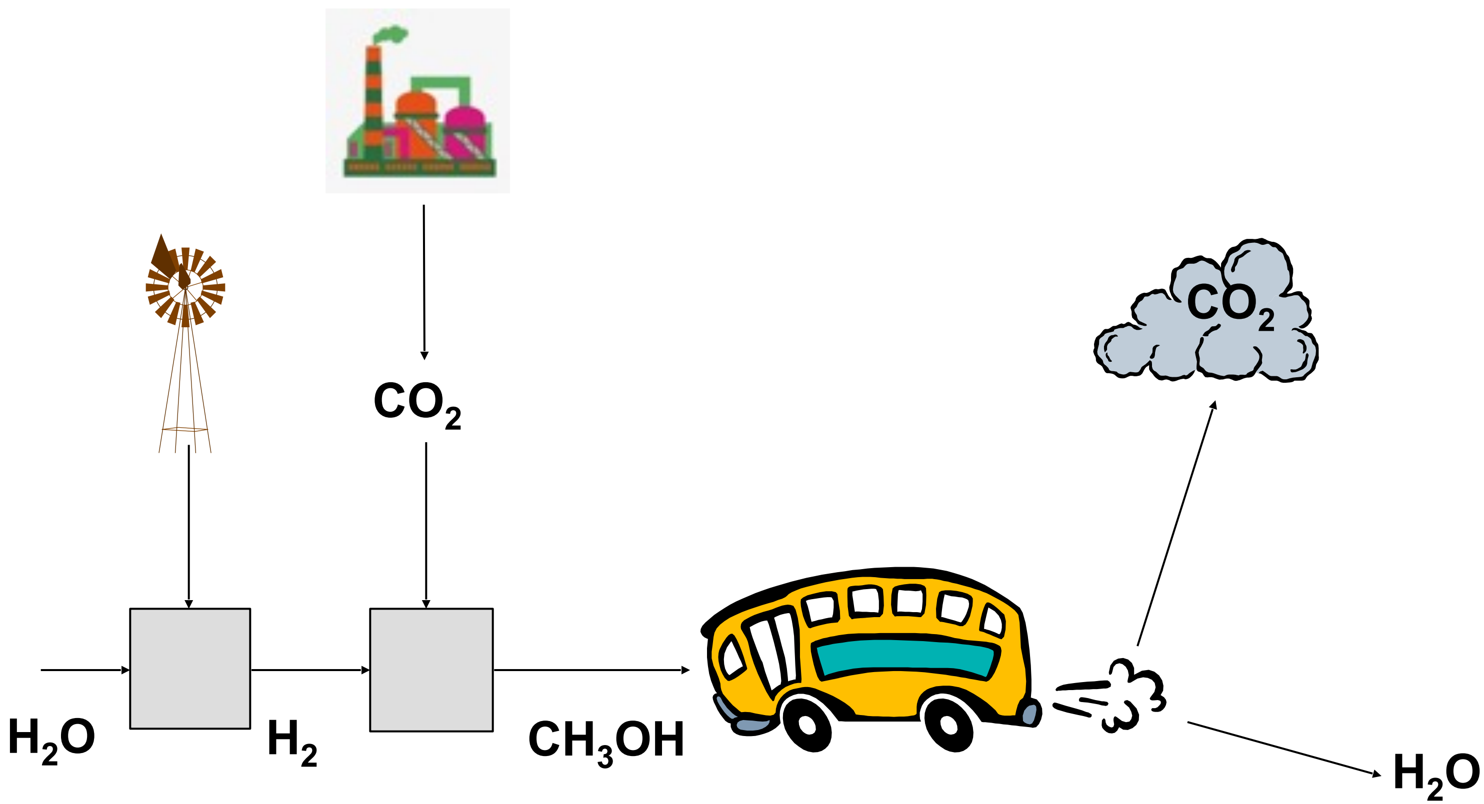

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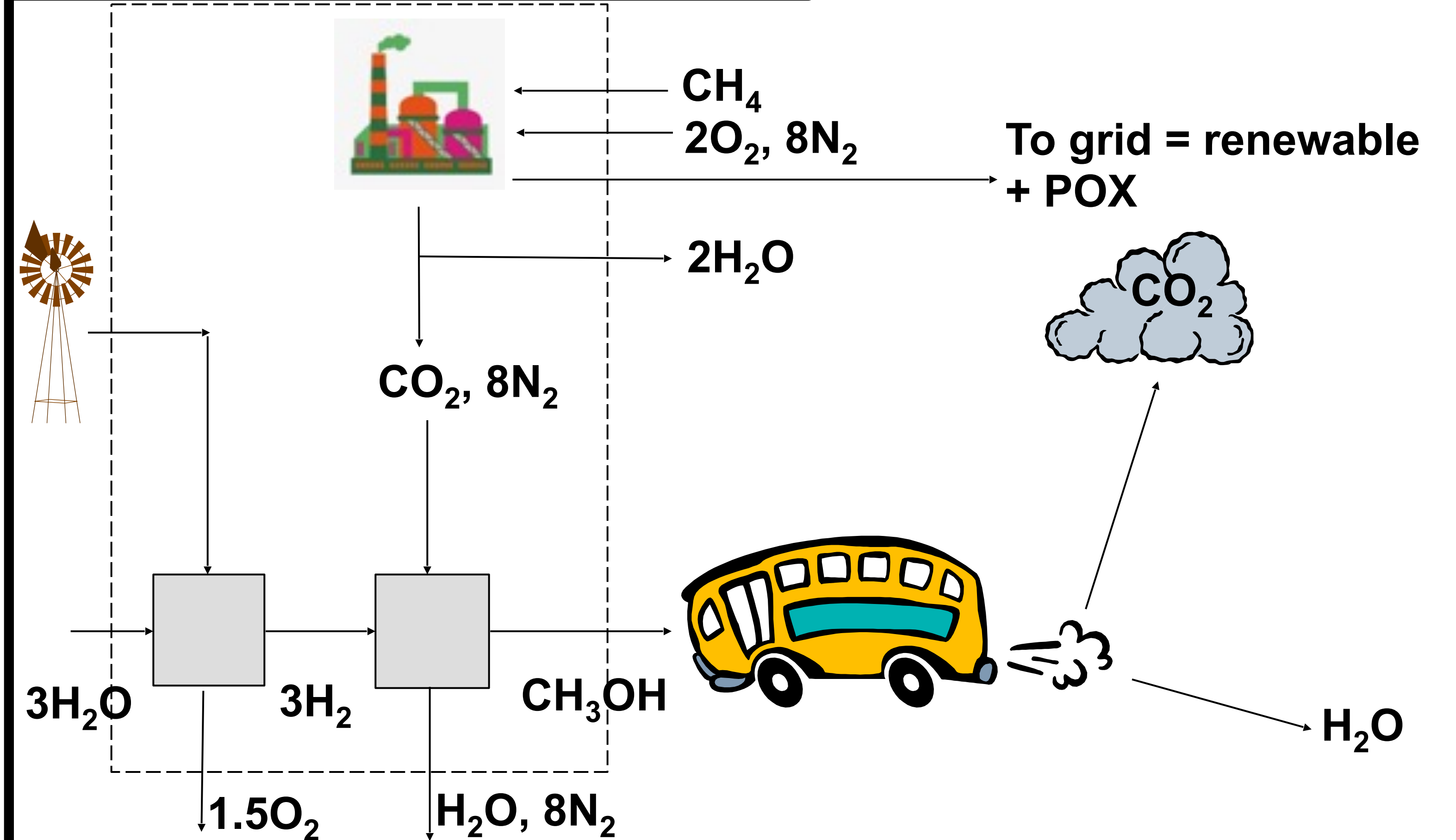

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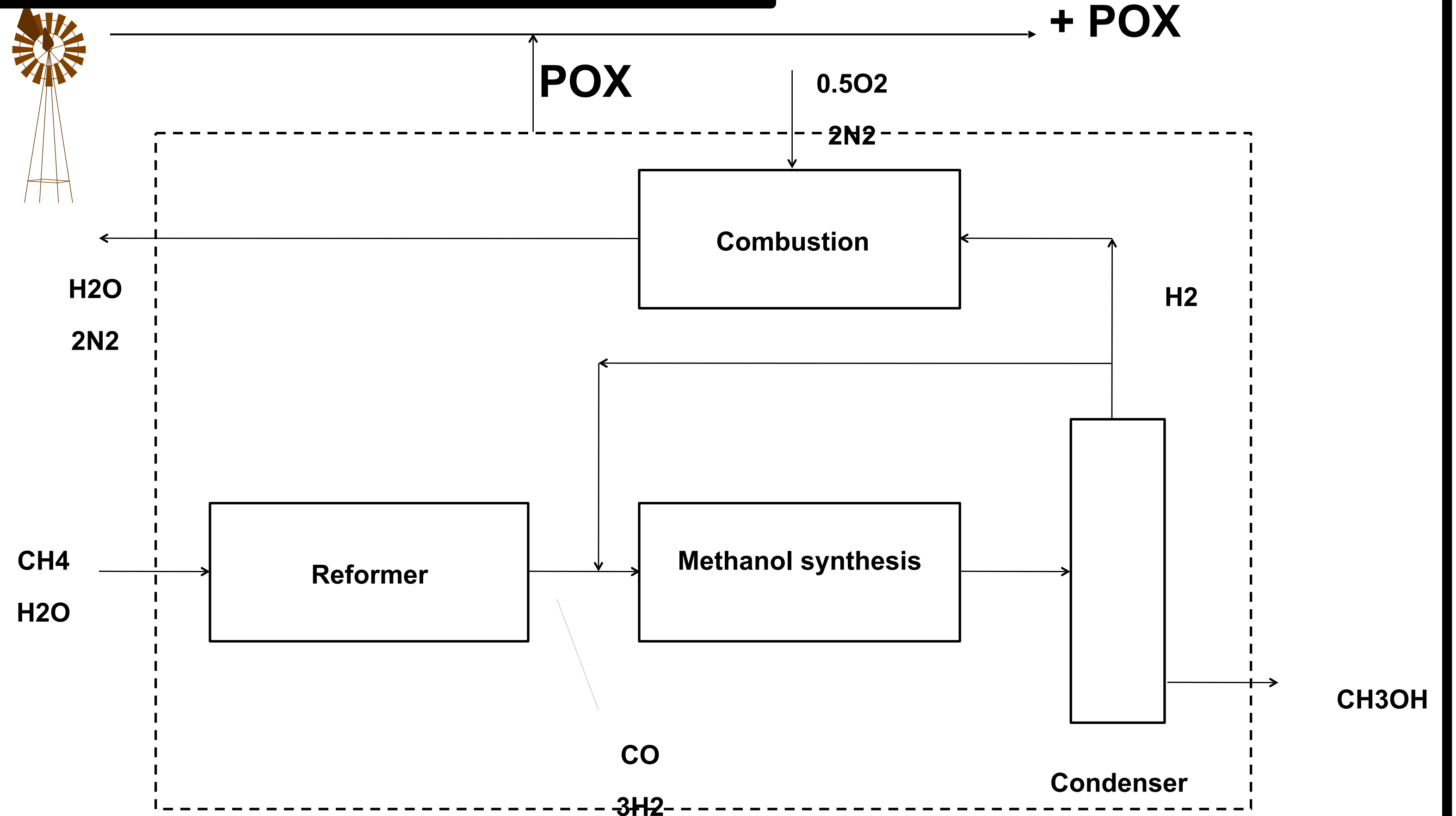

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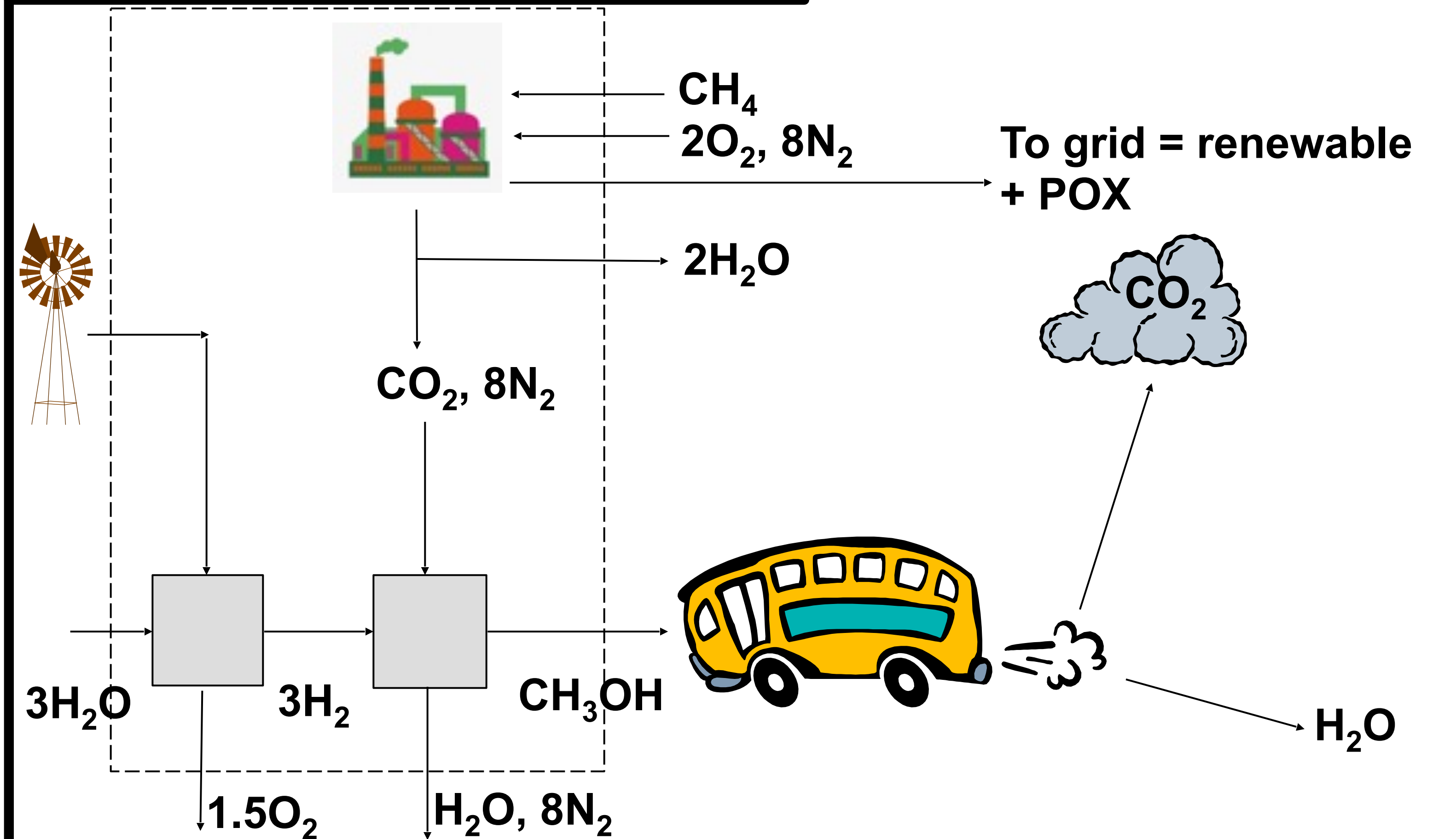
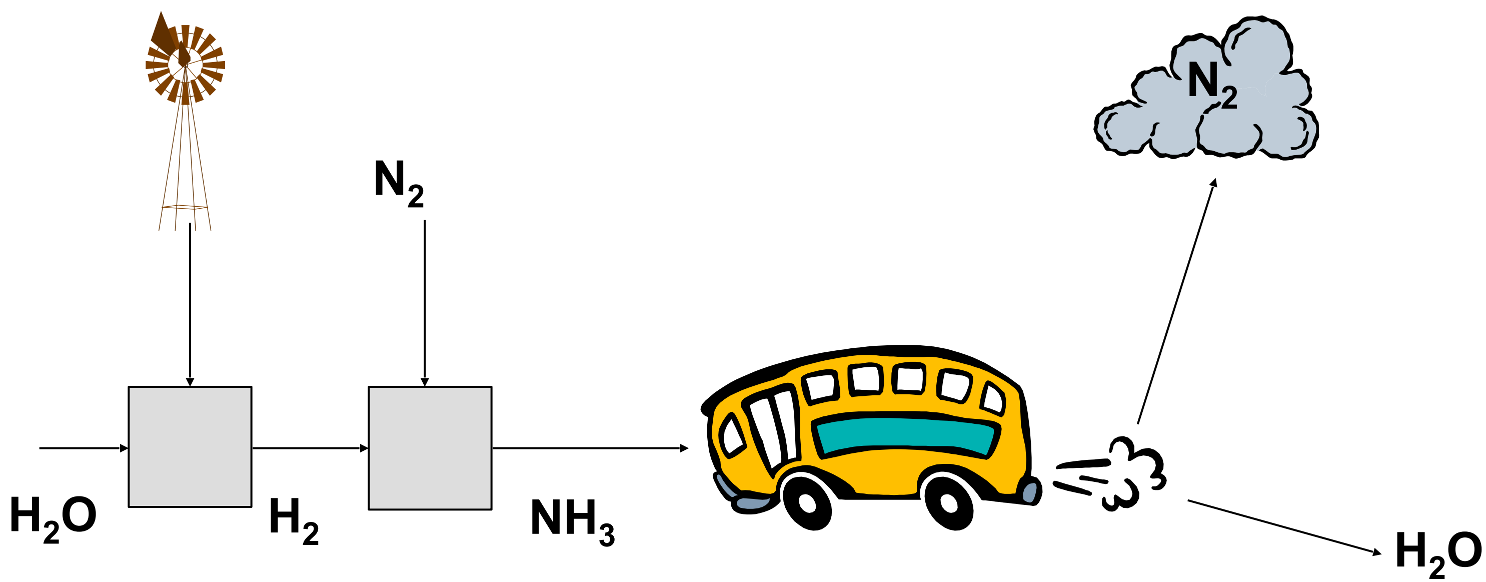


Methanol production from CO_2

- Better off learning how to ‘turn down’ power plants when renewable energy electricity is available
- Note we are simply using CO2 as a hydrogen carrier – we are utilising CO2 but not sequestering it – CCU but not CCS
- But can we not pick a better hydrogen carrier?

NH_3 for hydrogen storage/distribution



Heat of combustion of ammonia is about -320 kJ/mol, but MM is 17 compared with 32 for methanol (-700 kJ/mol)

How to estimate a heat of combustion

	ΔHf (298K) kJ/mol	ΔGf (298K) kJ/mol
$CO_2(g)$	-393	-394
$H_2O(g)$	-242	-228
$H_2O(l)$	-286	-235
$CH_3OH(g)$	-201	-161
$CH_3OH(l)$	-238	-166
$CH_4(g)$	-75	-51

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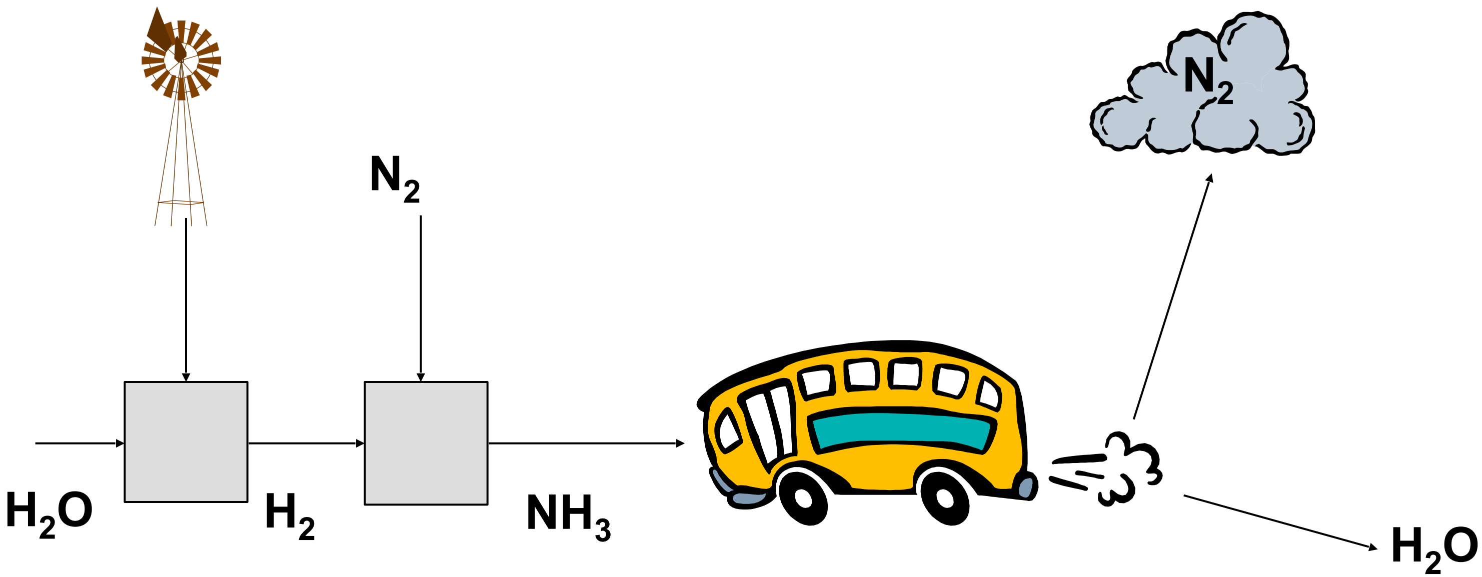

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H2**	142	1.73	infinite
NH3	18.8	13.7	infinite

*CH_4 - STP, LNG; **H_2 at 150 bars

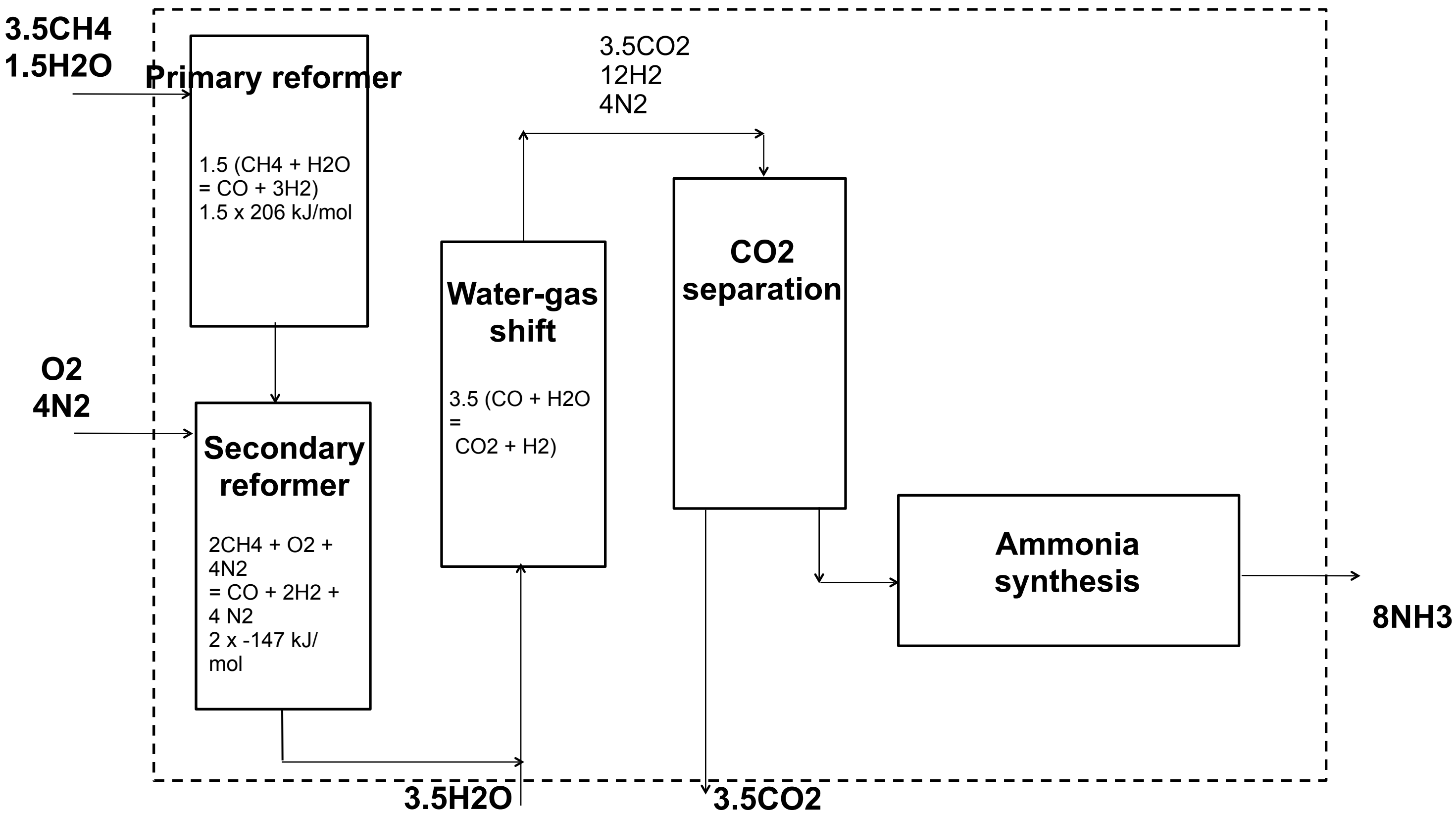
Distribution – CH_4 and organic liquids

H_2 – difficult to transport and store (will return to hydrogen)

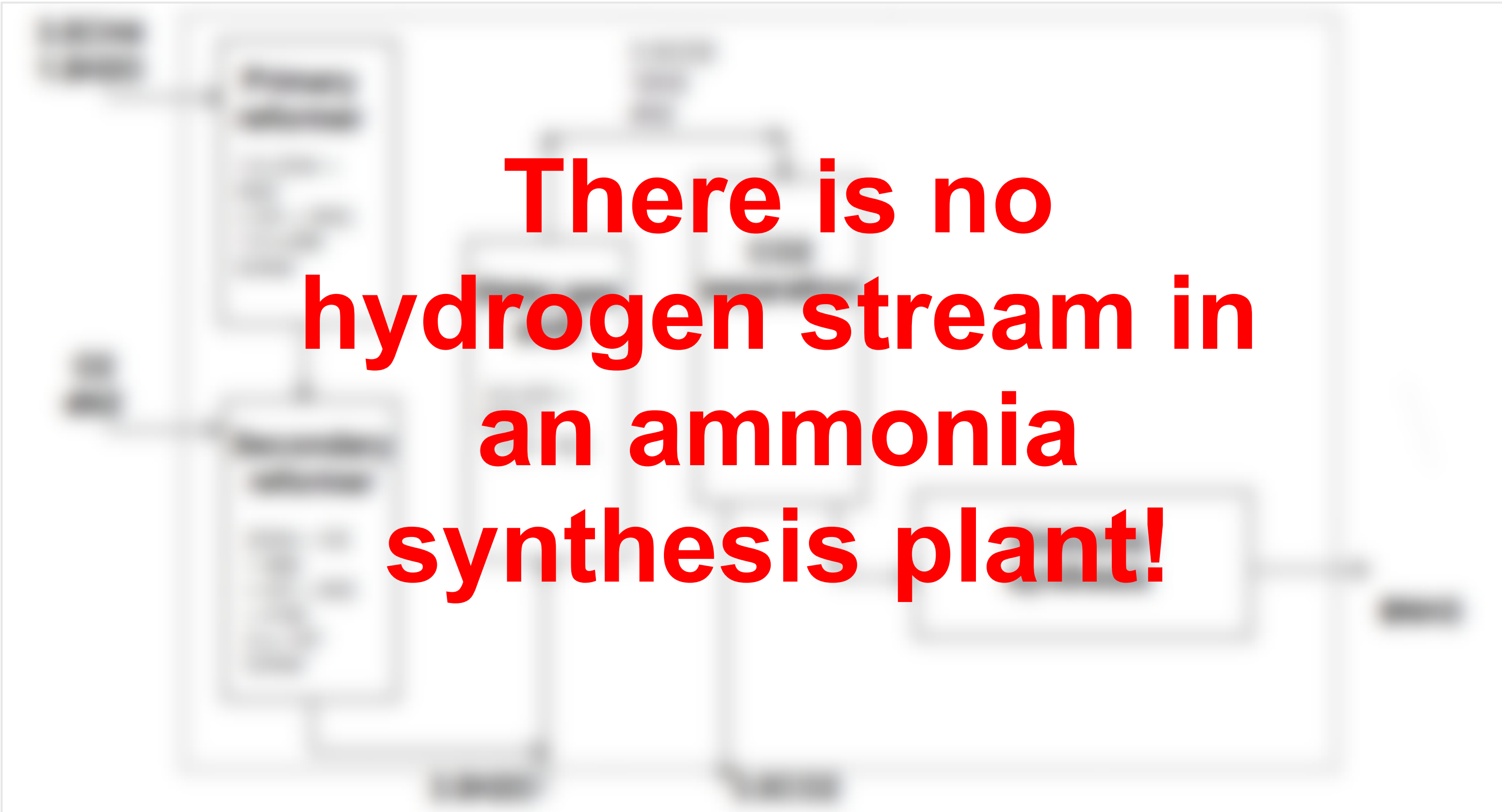
NH_3 for hydrogen storage/distribution

- NH3 – at 25°C vapour pressure is about 10 atm
- At ~ -30°C vapour pressure is about 1 atm
- Already move ammonia around in tankers
- Highly toxic – very easy to smell
- H_2 from electrolysis – how do be get ammonia, lot of nitrogen around but it happens to be mixed with oxygen!

NH_3 synthesis

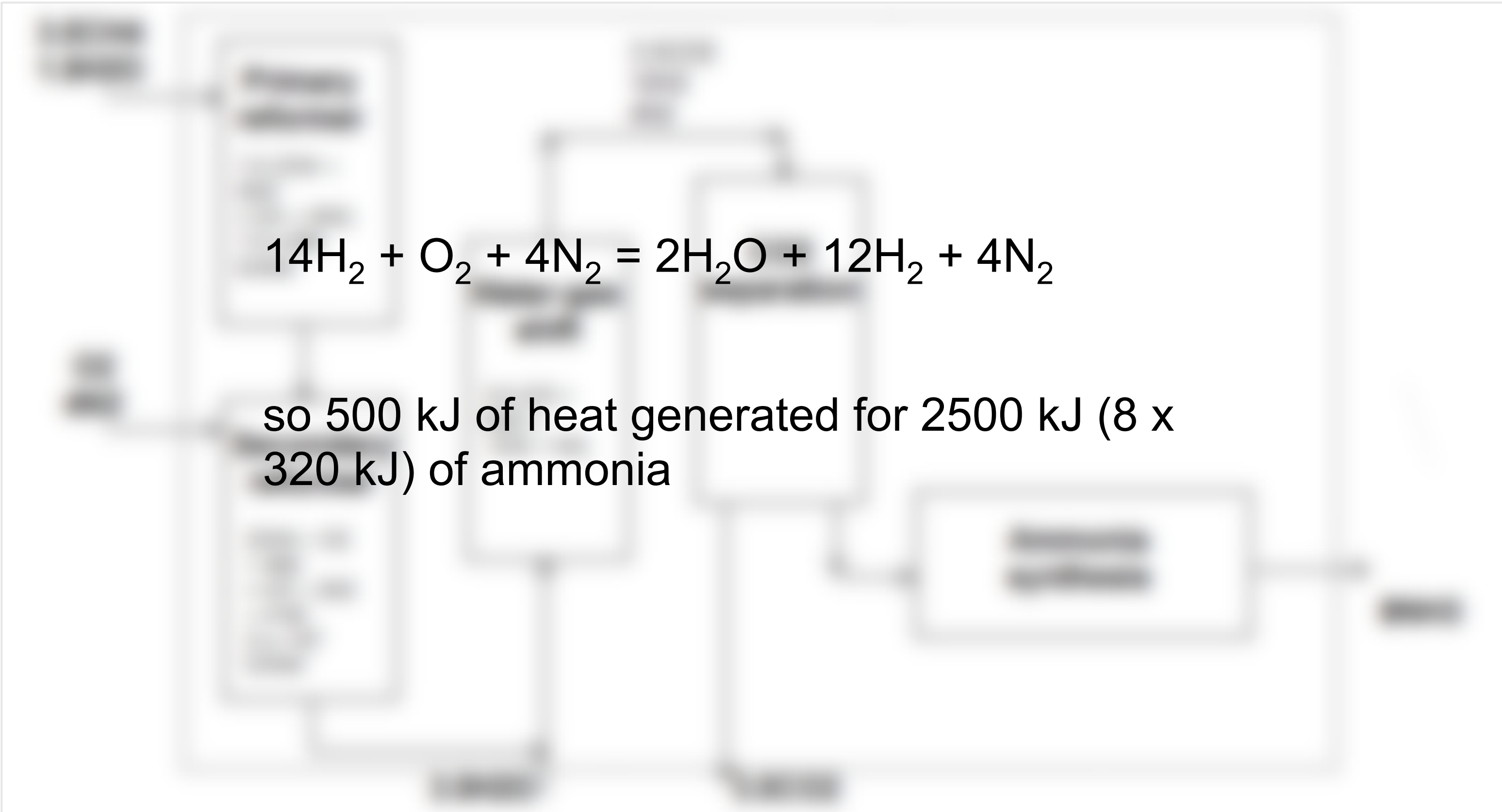


Methanol production from CO_2



There is no hydrogen stream in an ammonia synthesis plant!

NH_3 for hydrogen storage/distribution



$$14H_2 + O_2 + 4N_2 = 2H_2O + 12H_2 + 4N_2$$

so 500 kJ of heat generated for 2500 kJ (8 x 320 kJ) of ammonia

Better energy carrier

Look for a better chemical energy carrier

What about the rest of the system?

Energy conversion device

Energy conversion efficiencies:

Rule of thumb: internal combustion engine – 1/3 power, 1/3 cooling, 1/3 exhaust

Adiabatic fuel cell at max power output – 50% as electrical power, 50% exhaust

Why do we need cooling?

Adiabatic temperature rises for fuels

Most fuels are more or less $(CH_2)_n$

$6N_2 + 1.5\ O_2 + CH_2 = 6N_2 + H_2O + CO_2$

Adiabatic temperature rises in air are all around 2000 K

Cp ~ 7/2 R at for diatomic gas NPT

1000 K – 4R for N_2, 5R for H_2O, 6.5R for CO_2

Cp is 35.5R for stream, 300 kJ, heat of combustion is ~ 650 kJ

Adiabatic temperature rise ~ 2200 K

Hydrogen is slightly higher.

Adiabatic temperature rises for fuels

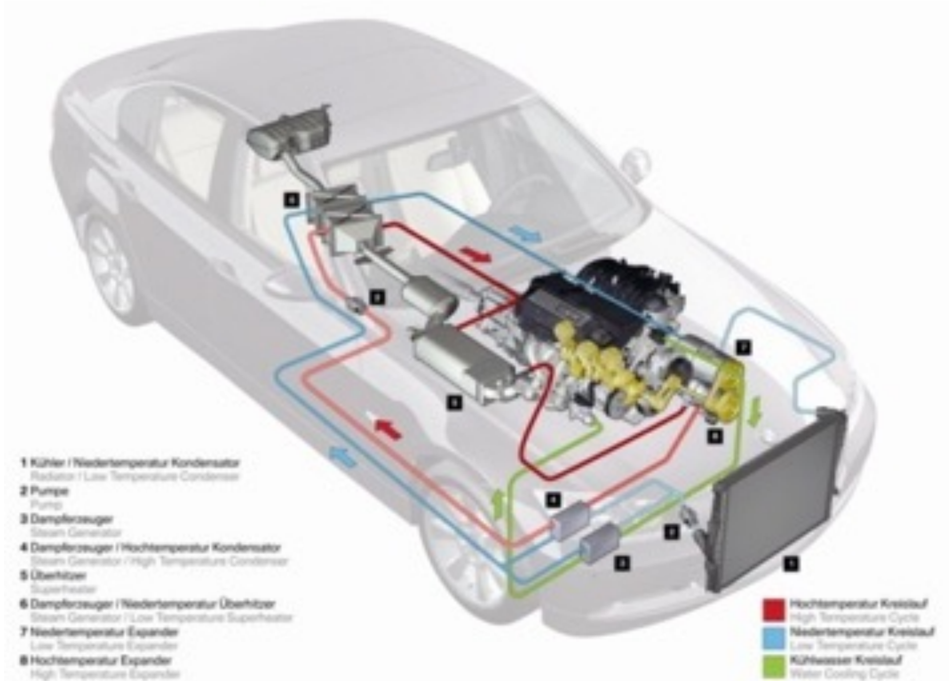
700 K temperature of device over ambient means 30% of energy lost in exhaust.

But need extra cooling if device cannot achieve 70% efficiency or it will overheat (if adiabatic)!

Fuel cells often need to run with extra air flow

Waste heat recovery

BMW turbosteamer – Rankine cycle for exhaust heat recovery. Increases overall efficiency by 15%.



http://www.heat2power.net/en__benchmark.php

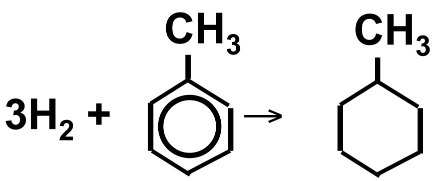
Integration with energy storage system

- We want a hydrogen carrier that requires heat input of about 75 kJ/mol of H_2 to release the hydrogen (0.3 x 250 kJ/mol H_2)

- This would allow us to shift waste heat off a vehicle and generate it at the hydrogenation facility

Hydrogen storage/distribution

At the hydrogen source:

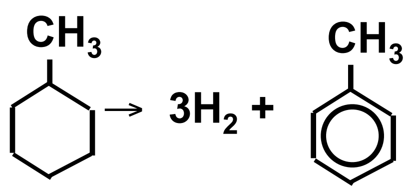


Toluene MCH

ΔH = -205 kJ/mol MCH or -70 kJ/mol H_2

ΔG = -98 kJ/mol MCH or -32 kJ/mol H_2

In the vehicle:



ΔH = +205 kJ/mol MCH or +70 kJ/mol H_2

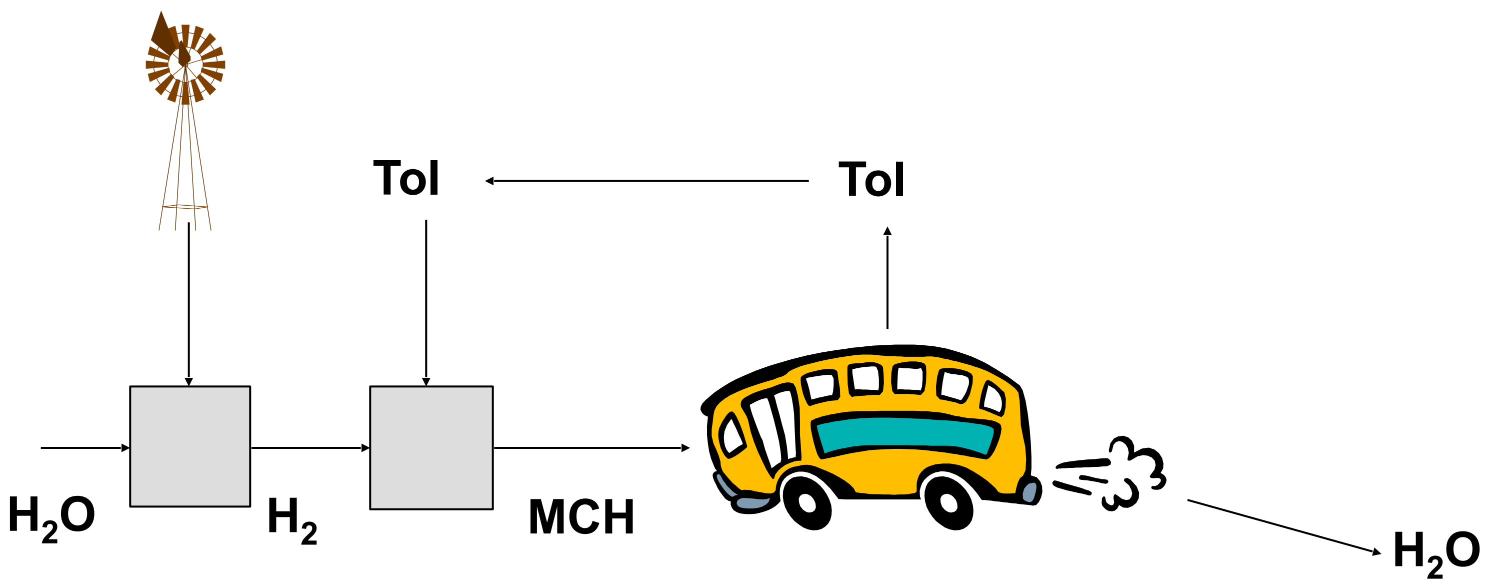
ΔG = +98 kJ/mol MCH or +32 kJ/mol H_2

Closed carbon cycle

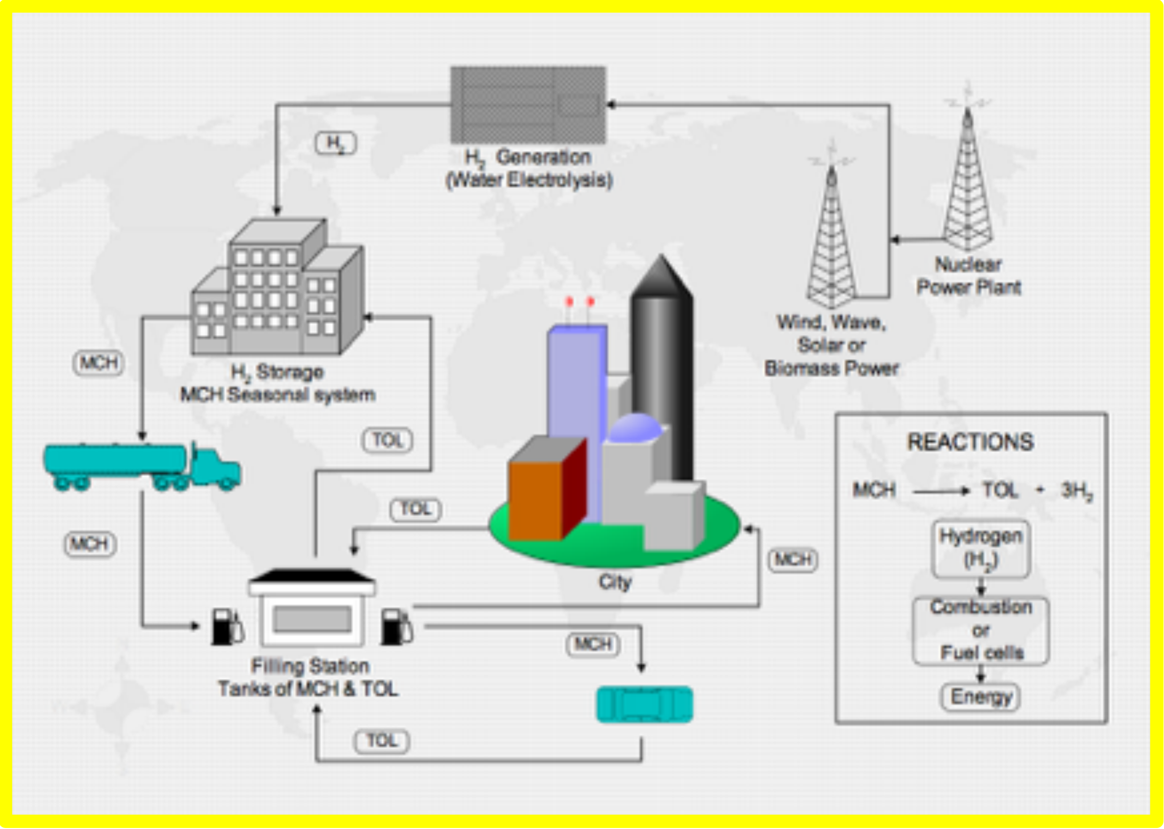
6.2 wt%

Hydrogen storage/distribution

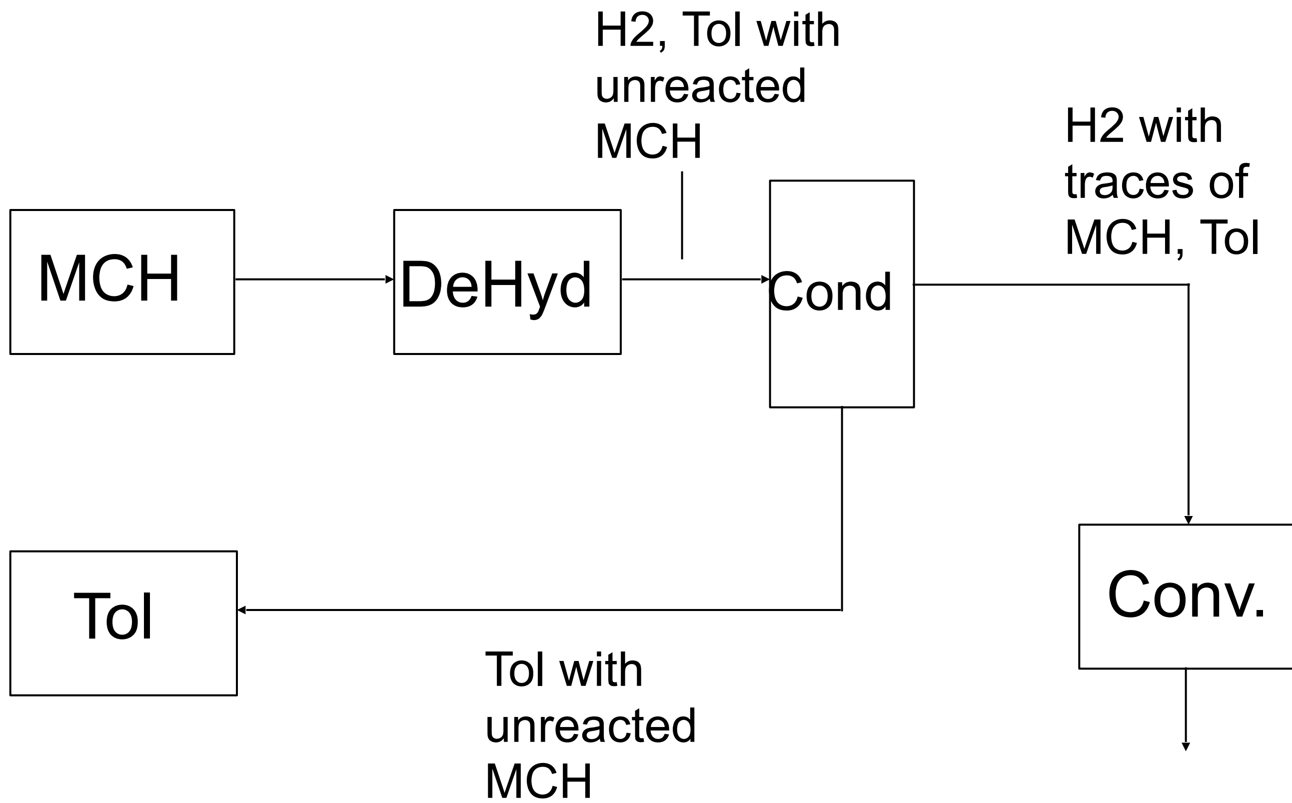
Closed carbon cycle:



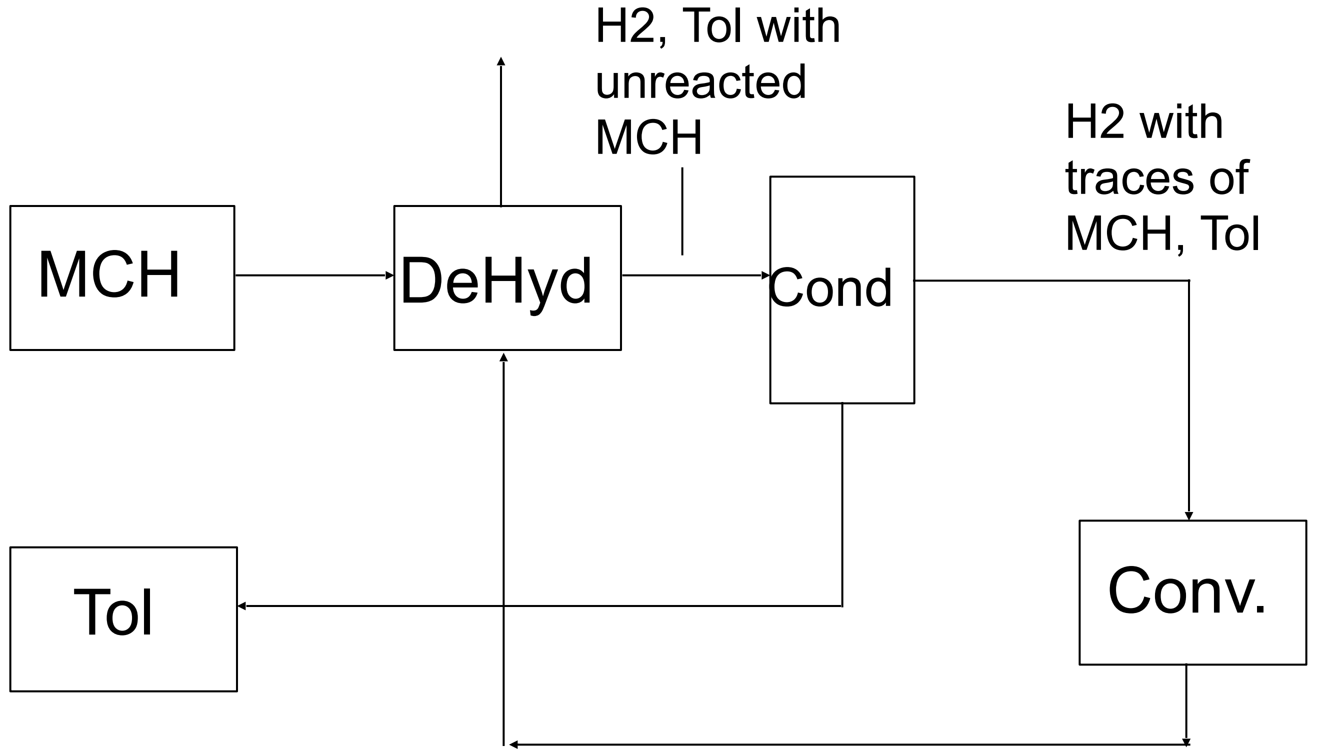
Hydrogen storage/distribution



MTH system


H2, Tol with unreacted MCH
H2 with traces of MCH, Tol
MCH
DeHyd
Cond
Tol
Conv.
Tol with unreacted MCH

MTH system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MTH/SOFC system – energy integration

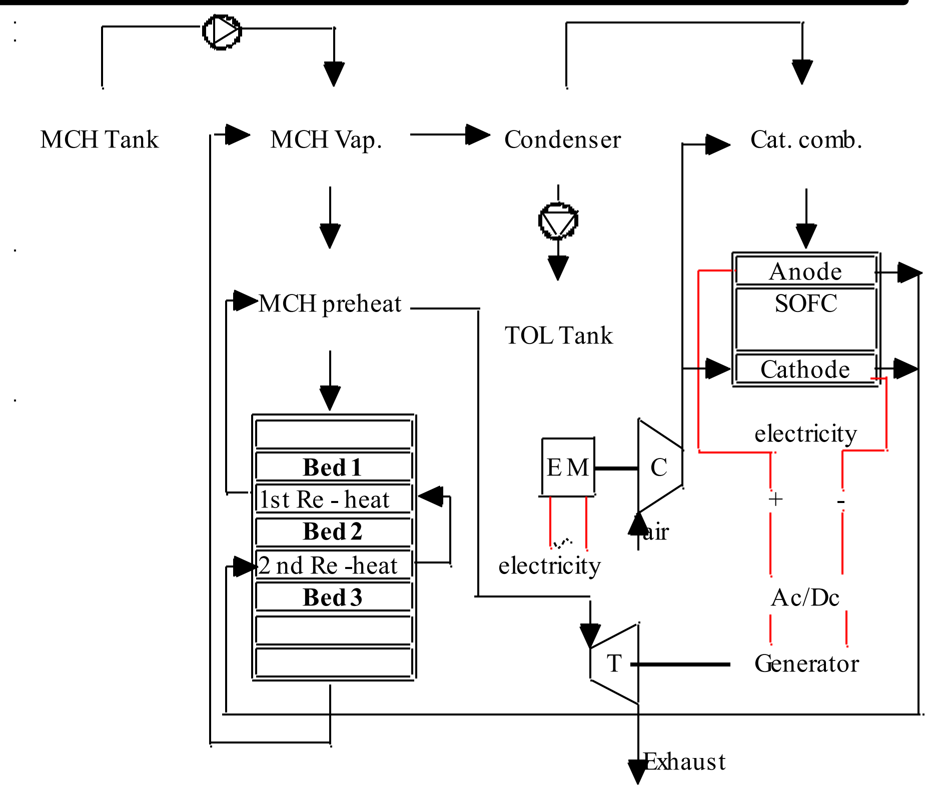

Figure 1 The Flow diagram for the MTH - SOFC system

MTH/SOFC system – energy integration

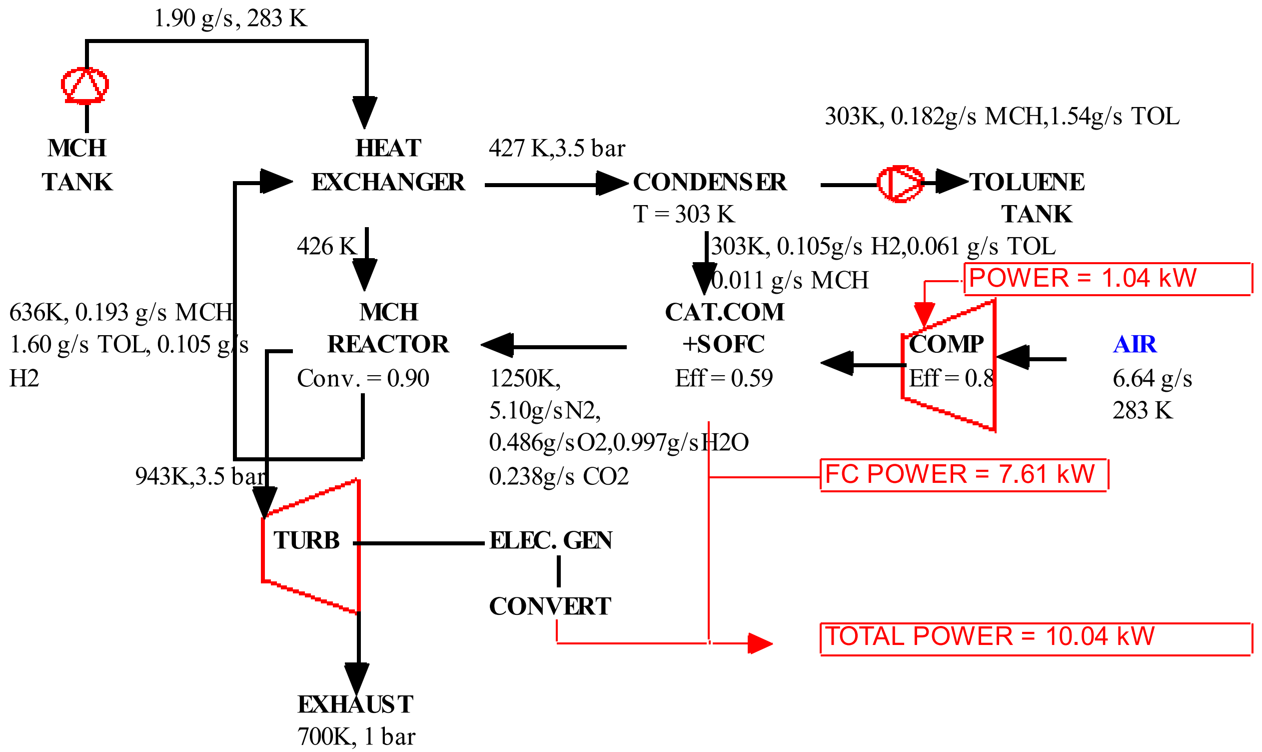

Figure 2 Mass flows and temperatures around the "base case" flowsheet.

MTH/SOFC system – pinch analysis

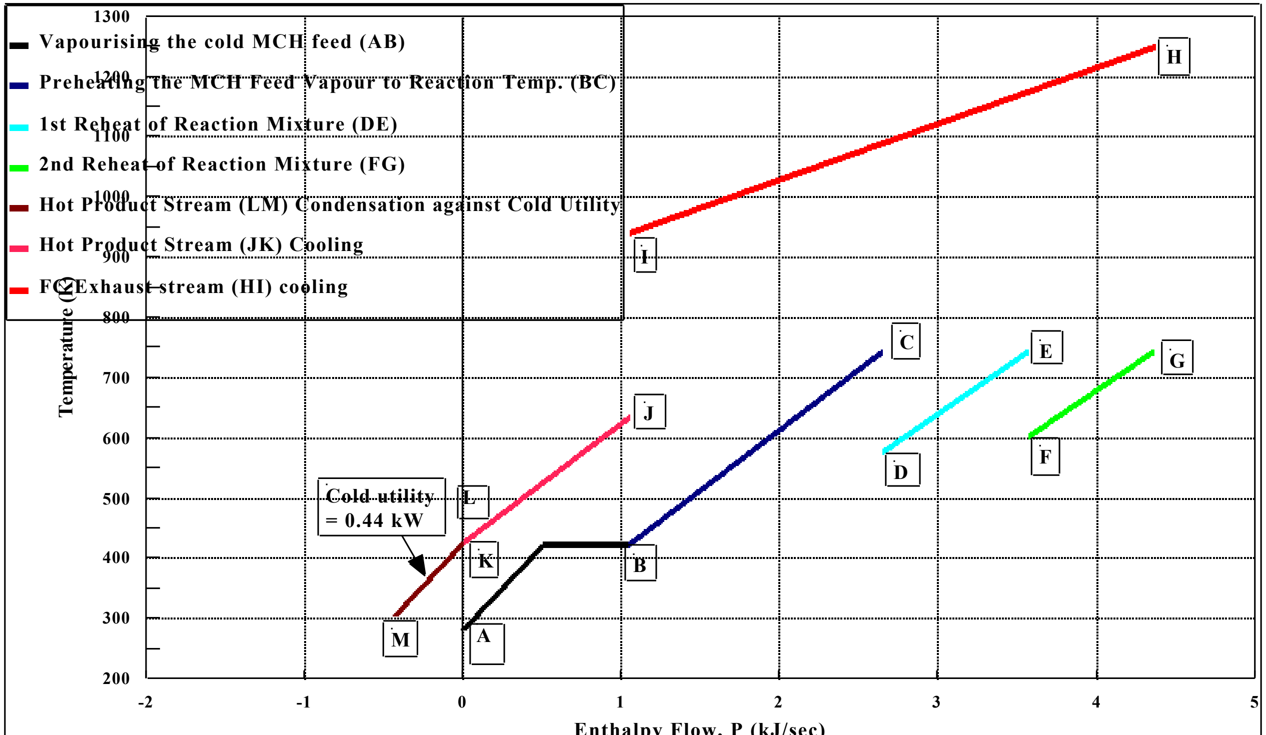

Figure.3 The Temperature - Enthalpy Flow Rate Diagram

MTH/SOFC system – pinch analysis

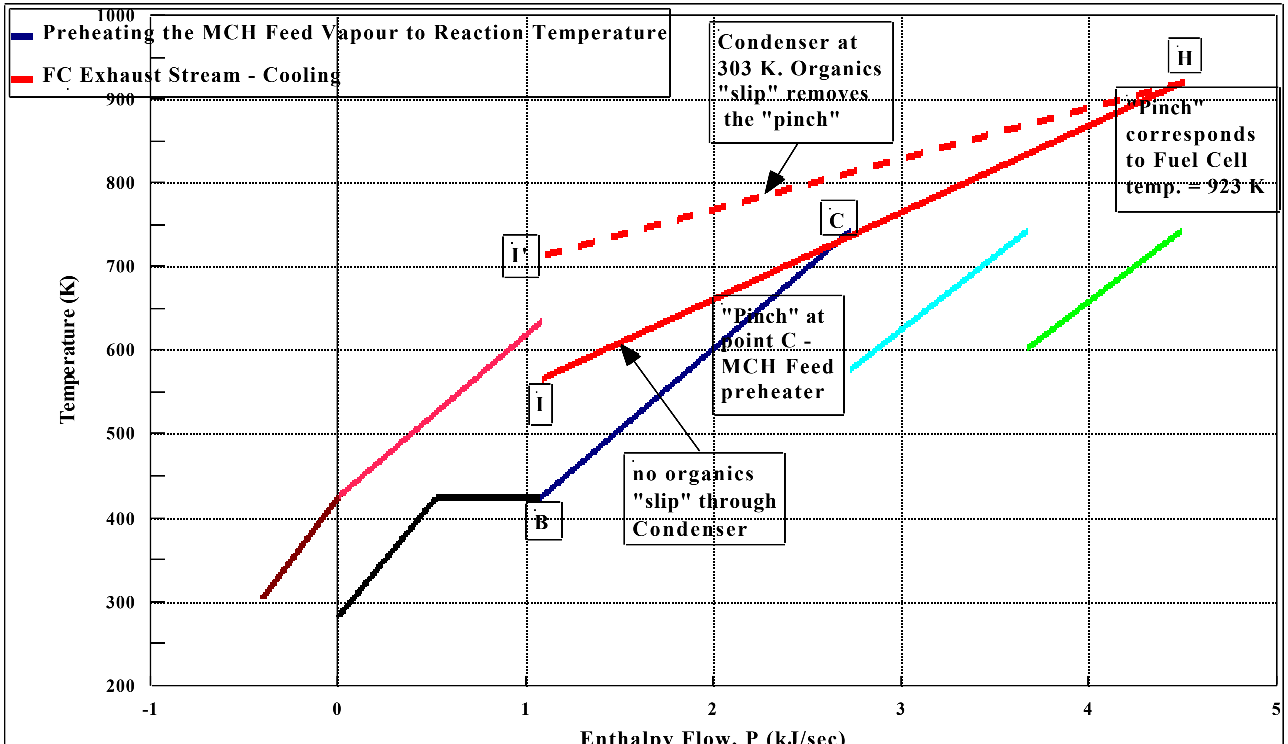

Figure 4 "Pinch" Analysis of the Heat Exchanger Network

Fuels

Fuel	MJ/kg	MJ/litre	kJ/mol CO2
CH4*	55.5	0.04/24.0	890
CH3OH	19.9	15.8	638
C2H5OH	26.8	21.2	618
Gasoline	46.8	34.1	~600
Coal	27	21	<600
H2**	142	1.73	infinite
MCH/Tol	8.8	7.0	2 000-20 000

*CH_4 - STP, LNG; **H_2 at 150 bars

Summary

- Could we ever have ‘clean’ hydrocarbon fuels?
- Case study of carbon dioxide to fuels – traps to avoid – must look at the whole energy system
- What about the waste heat from an automobile? Is there an opportunity? Match endothermic fuel processing step with available hot exhaust enthalpy. Shift ‘waste’ heat to stationary process.
- MTH system – 6 wt% equivalent hydrogen. Could use existing infrastructure.

Objective of this talk

- A chemical energy transformation is never 100% efficient – need to think about what to do about the inefficiencies and waste heat – whole system approach – simple view of e.g. energy densities is not sufficient
- Need a grasp of fundamental (but simple) thermodynamics
- Also simple process flowsheets including opportunities for heat transfer (awareness of how to match e.g. hot and cold streams)
- Don't think of hydrocarbons as dirty – it is the way we use them

END