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

Ian S. Metcalfe
School of Engineering
Newcastle University

15 May 2018
A short history of fossil fuels for chemical energy storage
A short history of fossil fuels for 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 collier – North of England

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

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

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

‘In 1870 Armstrong installed a Siemens dynamo in what was the world's first hydroelectric power station’
https://en.wikipedia.org/wiki/Cragside
➢ 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 CO2 emissions and a big improvement in engine efficiency
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

➢ Thermodynamics of production (exothermic versus endothermic)
➢ Purity issues
➢ Toxicity of carrier
➢ State and conditions of carrier
➢ Thermodynamics 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?

Readily available oxidant is oxygen

https://en.wikipedia.org/wiki/Periodic_table
How can we store chemical energy?

Large heats of reaction per unit mass, e.g., $2\text{Li} + \text{O} = \text{Li}_2\text{O}$. Ionic solids.

https://en.wikipedia.org/wiki/Periodic_table
How can we store chemical energy?

Reduction of Li$_2$O to Li again (charging the chemical energy store). How can we do that? Need something that will break Li$_2$O bonds – not easy – do it electrochemically
How can we store chemical energy?

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

I will not talk about batteries here
How can we store chemical energy?

Another solid store used throughout history.

https://en.wikipedia.org/wiki/Periodic_table
How can we store chemical energy?

Combination of light elements as chemical energy stores?

https://en.wikipedia.org/wiki/Periodic_table
How can we store chemical energy?

H₂, LiBH₄, NH₃, hydrocarbons (can be liquids at NTP)

https://en.wikipedia.org/wiki/Periodic_table
<table>
<thead>
<tr>
<th>Fuel</th>
<th>MJ/kg</th>
<th>MJ/litre</th>
<th>kJ/mol CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4*</td>
<td>55.5</td>
<td>0.04/24.0</td>
<td>890</td>
</tr>
<tr>
<td>CH3OH</td>
<td>19.9</td>
<td>15.8</td>
<td>638</td>
</tr>
<tr>
<td>C2H5OH</td>
<td>26.8</td>
<td>21.2</td>
<td>618</td>
</tr>
<tr>
<td>Gasoline</td>
<td>46.8</td>
<td>34.1</td>
<td>~600</td>
</tr>
<tr>
<td>Carbon</td>
<td>27</td>
<td>21</td>
<td>&lt;600</td>
</tr>
<tr>
<td>H2**</td>
<td>142</td>
<td>1.73</td>
<td>infinite</td>
</tr>
</tbody>
</table>

*CH4 - STP, LNG; **H2 at 150 bars

Distribution – CH₄ and organic liquids

H₂ – difficult to transport and store (will return to hydrogen)
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 Ignacy Lukasiewicz discovers how to distil oil.

1859 – Edwin L. Drake drills down 70 feet (21 meters) 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
➢ Combusted to produce CO2 and H2O.
➢ Why don’t we capture the CO2 to make ‘artificial’ hydrocarbon fuels? Hot research area!
➢ Case study of hydrogenation of carbon dioxide - CCU

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

C4-C12 → CO₂ → H₂O
Methanol production from CO₂

Methanol production using open carbon cycle:
Does it make sense?
Methanol production from CO₂
Methanol production from CO\(_2\):

1. \(3H_2O\) -> \(3H_2\)
2. \(3H_2\) + \(1.5O_2\) -> \(H_2O, 8N_2\)
3. \(H_2O, 8N_2\) + \(CO_2\) -> \(CH_3OH\)
4. \(CH_3OH\) + POX = \(H_2O\) (To grid = renewable + POX)
Methanol production from CO₂

To grid = renewable + POX

Methanol synthesis

Reformer

CO

H₂O

H₂O

2N₂

CH₄

0.5O₂

2N₂

Combustion

H₂

H₂O

2N₂

CH₃OH

Condenser

3H₂
Methanol production from CO$_2$

1.5O$_2$ → H$_2$O, 8N$_2$

H$_2$O → 2H$_2$O

CO$_2$, 8N$_2$ → CH$_4$

2O$_2$, 8N$_2$ → To grid = renewable + POX

3H$_2$O → CH$_3$OH
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?
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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \Delta H_f ) (298K) kJ/mol</th>
<th>( \Delta G_f ) (298K) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂(g)</td>
<td>-393</td>
<td>-394</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>-242</td>
<td>-228</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>-286</td>
<td>-235</td>
</tr>
<tr>
<td>CH₃OH(g)</td>
<td>-201</td>
<td>-161</td>
</tr>
<tr>
<td>CH₃OH(l)</td>
<td>-238</td>
<td>-166</td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>-75</td>
<td>-51</td>
</tr>
</tbody>
</table>
How to estimate a heat of combustion

<table>
<thead>
<tr>
<th></th>
<th>ΔHf (298K) kJ/mol</th>
<th>ΔGf (298K) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2(g)</td>
<td>-393</td>
<td>-394</td>
</tr>
<tr>
<td>H2O(g)</td>
<td>-242</td>
<td>-228</td>
</tr>
<tr>
<td>H2O(l)</td>
<td>-286</td>
<td>-235</td>
</tr>
<tr>
<td>CH3OH(g)</td>
<td>-201</td>
<td>-161</td>
</tr>
<tr>
<td>CH3OH(l)</td>
<td>-238</td>
<td>-166</td>
</tr>
<tr>
<td>CH4(g)</td>
<td>-75</td>
<td>-51</td>
</tr>
</tbody>
</table>
Heat of combustion of ammonia is about -320 kJ/mol, but MM is 17 compared with 32 for methanol (-700 kJ/mol)
### NH₃ for hydrogen storage/distribution

<table>
<thead>
<tr>
<th>Fuel</th>
<th>MJ/kg</th>
<th>MJ/litre</th>
<th>kJ/mol CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄*</td>
<td>55.5</td>
<td>0.04/24.0</td>
<td>890</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>19.9</td>
<td>15.8</td>
<td>638</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>26.8</td>
<td>21.2</td>
<td>618</td>
</tr>
<tr>
<td>Gasoline</td>
<td>46.8</td>
<td>34.1</td>
<td>~600</td>
</tr>
<tr>
<td>Carbon</td>
<td>27</td>
<td>21</td>
<td>&lt;600</td>
</tr>
<tr>
<td>H₂**</td>
<td>142</td>
<td>1.73</td>
<td>infinite</td>
</tr>
<tr>
<td>NH₃</td>
<td>18.8</td>
<td>13.7</td>
<td>infinite</td>
</tr>
</tbody>
</table>

*CH₄ - STP, LNG; **H₂ at 150 bars

Distribution – CH₄ and organic liquids

H₂ – difficult to transport and store (will return to hydrogen)
NH₃ 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
- H₂ from electrolysis – how do we get ammonia, lot of nitrogen around but it happens to be mixed with oxygen!
NH₃ synthesis

Primary reformer

3.5CH₄
1.5H₂O

1.5 (CH₄ + H₂O = CO + 3H₂)
1.5 x 206 kJ/mol

Secondary reformer

2CH₄ + O₂ + 4N₂
= CO + 2H₂ + 4 N₂
2 x -147 kJ/mol

Water-gas shift

3.5 (CO + H₂O = CO₂ + H₂)

CO2 separation

3.5CO₂
12H₂
4N₂

3.5H₂O
3.5CO₂

Ammonia synthesis

8NH₃
Methanol production from CO$_2$

There is no hydrogen stream in an ammonia synthesis plant!
14H₂ + O₂ + 4N₂ = 2H₂O + 12H₂ + 4N₂

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 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?
Most fuels are more or less \((\text{CH}_2)_n\)

\[6\text{N}_2 + 1.5 \text{O}_2 + \text{CH}_2 = 6\text{N}_2 + \text{H}_2\text{O} + \text{CO}_2\]

Adiabatic temperature rises in air are all around 2000 K

\(\text{Cp} \sim 7/2 \text{R at for diatomic gas NPT}\)

1000 K – 4R for N\(_2\), 5R for H\(_2\)O, 6.5R for CO\(_2\)

\(\text{Cp is 35.5R for stream, 300 kJ, heat of combustion is } \sim 650 \text{ kJ}\)

Adiabatic temperature rise \(\sim 2200 \text{ K}\)

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
We want a hydrogen carrier that requires heat input of about 75 kJ/mol of H\textsubscript{2} to release the hydrogen (0.3 x 250 kJ/mol H\textsubscript{2}).

This would allow us to shift waste heat off a vehicle and generate it at the hydrogenation facility.
At the hydrogen source:

\[ 3H_2 + \text{Toluene} \rightarrow \text{MCH} \]

\[ \Delta H = -205 \text{ kJ/mol MCH or } -70 \text{ kJ/mol H}_2 \]

\[ \Delta G = -98 \text{ kJ/mol MCH or } -32 \text{ kJ/mol H}_2 \]

In the vehicle:

\[ \text{MCH} \rightarrow 3H_2 + \text{Toluene} \]

\[ \Delta H = +205 \text{ kJ/mol MCH or } +70 \text{ kJ/mol H}_2 \]

\[ \Delta G = +98 \text{ kJ/mol MCH or } +32 \text{ kJ/mol H}_2 \]

Closed carbon cycle 6.2 wt%
Closed carbon cycle:

H₂O → H₂ → MCH → Tol

H₂O
Hydrogen storage/distribution
MCH DeHyd Conv. Tol

MCH

DeHyd

Cond

Tol

Conv.

H2, Tol with unreacted MCH

Tol with unreacted MCH

H2 with traces of MCH, Tol
MCH

DeHyd

Cond

Tol

Conv.

H₂, Tol with unreacted MCH

H₂ with traces of MCH, Tol

MTH system
Figure 1 The Flow diagram for the MTH - SOFC system
Figure 2 Mass flows and temperatures around the "base case" flowsheet.
Figure 3 The Temperature - Enthalpy Flow Rate Diagram
Figure 4 "Pinch" Analysis of the Heat Exchanger Network
<table>
<thead>
<tr>
<th>Fuel</th>
<th>MJ/kg</th>
<th>MJ/litre</th>
<th>kJ/mol CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄*</td>
<td>55.5</td>
<td>0.04/24.0</td>
<td>890</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>19.9</td>
<td>15.8</td>
<td>638</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>26.8</td>
<td>21.2</td>
<td>618</td>
</tr>
<tr>
<td>Gasoline</td>
<td>46.8</td>
<td>34.1</td>
<td>~600</td>
</tr>
<tr>
<td>Coal</td>
<td>27</td>
<td>21</td>
<td>&lt;600</td>
</tr>
<tr>
<td>H₂**</td>
<td>142</td>
<td>1.73</td>
<td>infinite</td>
</tr>
<tr>
<td>MCH/Tol</td>
<td>8.8</td>
<td>7.0</td>
<td>2 000-20 000</td>
</tr>
</tbody>
</table>

*CH₄ - STP, LNG; **H₂ at 150 bars
Could we ever have ‘clean’ hydrocarbon fuels?

Case study of carbon dioxide to fuels – traps to avoid – must look at the whole energy system


MTH system – 6 wt% equivalent hydrogen. Could use existing infrastructure.
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