Transitioning to a Hydrogen Energy Economy with the Help of Natural Gas

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Eric McFarland, Horia Metiu, Mike Gordon, Mike Doherty
Today’s Prosperity Is Powered By Low Cost Fossil Fuels

~ 770 Billion Tons CO$_2$/year from nature
~ 35 Billion Tons CO$_2$/year from us

In the meantime we are at risk for adverse environmental effects

Future Prosperity Will be Powered By Low Cost Nuclear Power +/- Low Cost Renewables
Forget the Scientists: Ask the people who have something to lose if they get it wrong

Global Insured Losses: Primarily weather related natural catastrophes!

Thanks to Mark Way, Head of Sustainability & Risk Assessment, Swiss Re

Source: sigma 2/2015
Economics Will Always Determine The Fuel Economy

Where would we be if cheap gas was not available?
Conventional Wisdom

according to an assessment by the IPCC, an intergovernmental climate-science body, oil and gas production needs to fall by about 20% by 2030 and by about 55% by 2050, in order to stop the Earth’s temperature rising by more than 1.5°C above its pre-industrial level.

But does it?  
Can it?  
...... should it?
On earth, coal, oil, and gas is where Nature stored solar energy for free. **Prediction:** Methane will be the most important molecule for the next century’s prosperity.

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**Gas That Makes a Mountain Breathe Fire Is Turning Up Around the World**

A group of scientists have found unusual types of methane escaping from the deep earth in hundreds of locations.
Building on what we know and already have

→ over 2 million miles of high pressure natural gas pipelines, the world’s largest “battery”

0.25 Mtons
$10^{10}$ MJ
~ 100MW-y
A Cost-Effective Transition Strategy (Plan B): Pyrolysis $\text{CH}_4 \rightarrow \text{H}_2 + \text{Carbon}$

- 35 Trillion kg $\text{CO}_2$
- 9.5 Trillion kg C
- 4.5 Trillion kg $\text{H}_2$
- 0.55 Trillion GJ
- 17,000 GW
- $\sim$2.8 Trillion kg Natural Gas

Increase Gas Production 7x
Outline:

• Pyrolysis of natural gas is the best option for CO$_2$-free hydrogen production.
• Pyrolysis thermochemistry and kinetic limits.
• UCSB technology makes possible reactive separation of H$_2$ from solid carbon in high temperature liquids.
On Earth, H₂ comes from (came from) Water

It’s about which electrons you want to move

>4.6 MW/kta H₂

H₂O → Hydrolysis Electrolysis → ½ O₂ → H₂

Energy Conversion (storage)

>1 MW/kta H₂

CH₄ + 2H₂O → Reforming and WGS → 4H₂ → CO₂

Fuel Production is Resource Refining (consumption)

>0.6 MW/kta H₂

CH₄ → Pyrolysis → 2H₂ → Cₐₙ₂

No Escaping Thermodynamics → Energy Input Needed!
Large Scale, Low-Cost, Hydrogen?

Cost = OpX + CapX

$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$

$\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C}_\text{solid}$

$\text{H}_2 \rightarrow \frac{1}{2} \text{O}_2$

$>0.6 \text{ MW/kta H}_2$

$>1 \text{ MW/kta H}_2$

$>4.6 \text{ MW/kta H}_2$

Economics Wins

$\sim$1-2M/kta H$_2$

~$4-8M/kta H$_2$

($\sim$1-2/Watt)

Cost = OpX + CapX

Large Scale, Low-Cost, Hydrogen?
Large Scale, Low-Cost, CO$_2$-free Hydrogen?

Must have: Negative value for CO$_2$
AND/OR Positive value for C (relatively small market)
Reversible Endothermic Reaction Favors High T, Low P

\[ CH_4 \leftrightharpoons C + 2H_2 \]

For Economics
Need High Rate
And High P

\[
\text{rate} \sim \left( k_f P_{CH_4} - k_r \left[ C_{S}^{*} \right] P_{H_2}^n \right)
\]

\[
r_{Ave} > \sim 1 \, \frac{\text{mole}}{m^3 - s}
\]
Seemingly Simple Chemistry

\[ \text{CH}_4 \rightleftharpoons C + 2\text{H}_2 \]

The Carbon “Problem”
Methane Pyrolysis by Reactive Separation of Carbon in High Temperature Catalytic Liquid Bubble Columns

- High Reaction Rate
- Separable Carbon

*Science 358, 917–921 (2017)*
Challenge #1: High Reaction Rate

Target: \( V < \sim 1 \text{ m}^3/\text{kta} \sim 1 \text{ m}^3/\text{mole/s} \)

\[ r(\text{mole/m}^3\cdot\text{s}) > 1 \]

C-H bond activation is rate limiting
High Temperature Liquid Metals

Fundamentally different reactive surfaces

Molten Metals Stable at 700-1100 C in H₂

Low Cost Acceptable Toxicity

Conductors High Surface Tensions

Active CH₄ Catalyst

Separable C

Pt

W

Al

?
Activity for Methane Pyrolysis Varies With Melt Composition, $P_M=0.1\text{atm}$

- At solubility limit

1000 °C

Liquid

Liquid pure

Liquid Ni alloys

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>2.E+00</td>
</tr>
<tr>
<td>Bi</td>
<td>0.00</td>
</tr>
<tr>
<td>Sn</td>
<td>0.02</td>
</tr>
<tr>
<td>Ga</td>
<td>0.04</td>
</tr>
<tr>
<td>Ag</td>
<td>0.06</td>
</tr>
<tr>
<td>Pure Pb</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Pt-Sn</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Pt-Bi</td>
<td>0.17</td>
</tr>
<tr>
<td>62% Pt-Bi</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Ni-In</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Ni-Sn</td>
<td>0.17</td>
</tr>
<tr>
<td>73% Ni-In</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Ni in Ga</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Ni in Pb</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Ni in Bi</td>
<td>0.17</td>
</tr>
<tr>
<td>27% Ni in Au</td>
<td>0.17</td>
</tr>
<tr>
<td>27% Ni in Bi</td>
<td>0.17</td>
</tr>
<tr>
<td>27% Ni in Bi</td>
<td>0.17</td>
</tr>
<tr>
<td>17% Cu in Sn</td>
<td>0.17</td>
</tr>
</tbody>
</table>

0.25 sccm CH₄
2.5 sccm Ar

Ches Upham

Clarke Palmer

0845334118

8 mm OD, 1 mm ID Quartz inlet tube
8 mm alumina crucible
12 mm outer quartz tube

Gas out to mass spectrometer

Quartz

Quartz
Activity for Methane Pyrolysis Varies, (but not tremendously), With Melt Composition: the Solid Carbons are Different

$T = 1000^\circ C$

$P_M = 0.1\text{atm}$

**Graph:**
- TOF [s$^{-1}$] vs. Melt Composition
- 50 mol% Sn-Bi, 50 mol% Ag-Bi, 45 mol% Mn-Bi, 33 mol% Ni-Bi, 45 mol% Cu-Bi
- Raman Shift (cm$^{-1}$) vs. Intensity [a.u.]

**Raman Shift Graph:**
- Peaks labeled D and G
- Intensity range from 0 to 30
Ab initio molecular dynamics calculations support charge transfer from host (Bi) to the electrophile (Ni)

\[
\begin{align*}
\text{Bi}^{\delta+} & \xrightarrow{e^{-}} \text{Bi}^{\delta+} \\
\text{Ni}^{-} & \xrightarrow{e^{-}} \text{Bi}^{\delta+} \\
\text{Bi}^{\delta+} & \xrightarrow{e^{-}} \text{Bi}^{\delta+} \\
\end{align*}
\]
Variable Residence Time, Pressure, Temperature, in Ni:Bi Bubble Columns

![Image of orange liquid in tube]

**Graph (b):**
- **Ln [rate (mol / cm² s)]** vs. **P_{CH4} (kPa)**
- **Slope = 0.97**
- **1000 °C**
- **1st order**
- **Methane**
- **Hydrogen / 2**

**Graph (c):**
- **Ln [P_{CH4} (kPa)]** vs. **P_{CH4} (kPa)**
- **Hydrogen**
- **Ethane + Ethene**
- **Aromatics + Acetylene**

First Order in P_{CH4}
High H₂ Selectivity

Measured (red dotted)
Modeled (black line)
~ 1 meter bubble column → 95% methane conversion to H₂ at 1060°C

*Rubbia, et. al., 2016

Science 358, 917–921 (2017)

<table>
<thead>
<tr>
<th></th>
<th>Tin*</th>
<th>Ni-Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1175 ºC</td>
<td>1060 ºC</td>
</tr>
<tr>
<td>Height (m)</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Conversion</td>
<td>78%</td>
<td>95%</td>
</tr>
<tr>
<td>Equilibrium conversion</td>
<td>99%</td>
<td>98%</td>
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</table>

maximum 15 sec space time, 2% gas-phase holdup

95% (1060°C)

86% (1030°C)

1.4 atm CH₄
0.35 atm Ar
High Temperature Molten Salts

Fundamentally different reactive surfaces

Molten Salt Catalysis of Gas Reactions

C. N. Kenney
Department of Chemical Engineering
Cambridge University
Cambridge, England

Catalysis Rev. 11:1, 197-224, 1975

Molten Salts Stable at 700-1100°C in H₂

Active CH₄ Catalyst

Separable C

Low Cost Acceptable Toxicity

Halides

Carbonates

Nitrates

Insulators Low Surface Tensions
Monovalent salts have similar (relatively low) activities

<table>
<thead>
<tr>
<th></th>
<th>KCl</th>
<th>NaBr</th>
<th>NaCl</th>
<th>KBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ea } [\text{kJ/mole}])</td>
<td>280</td>
<td>270</td>
<td>300</td>
<td>330</td>
</tr>
</tbody>
</table>
Defect Free Monovalent Alkali Halide Salts Are (unreactive) Insulators!

Filled states

Nowhere to bind

H$_3$C-H

Heterolytic H$_3$C$^+$/H-$^+$

Homolytic H$_3$C$^*$H$^*$

M$^+$/A$^-$

Lewis Acid/Base Pair

MgO(Li) Empty O Lewis Acid site →

1000°C
Methane

1000°C

Argon
High methane conversion observed in several divalent salts

*molten KF–MgF$_2$ bubble column at short residence time*
High Activity Observed in Molten MnCl$_2$-based salts
activity correlates to tetrahedrally coordinated MnCl$_4^{2-}$ molecular ion.

In Press
Applied Catalysis B: Environmental

Gas Phase Homogeneous
Melt Surface Heterogeneous
MnCl$_2$–based Melts Produce Graphitic Carbon, Not Possible In Gas Phase
Far Greater Hydrogen Selectivity (>98%) at 40% Methane Conversion on MnCl$_2$

1) High activity
2) H/D exchange to CD$_2^+$
3) Graphitic Carbon
4) Minimal gas phase intermediates

=> Heterogeneous surface reaction
Overall, several candidate catalytic melts have sufficient rates.
Make Lots of Carbon!

~1 Million Tons per year ~ 1 GW_{\text{Thermal}}

2018 Global Market
~ 50 M tons/y

~$1000/ton

~$200/ton

(-$15)/ton
Different C morphologies observed in different melts under different conditions

- **spheres**
- **Rods/fibers**
- **particles**
- **sheets**
Carbon Purity from Liquid Metals Has Been Challenging

Commercial Carbon Is Not Always Pure (but the best C is)

**Mined Graphite:**
Madagascar: 85-90% carbon
Canada: 90-97% carbon
China 90-96% carbon

**Coconut Shell Carbon (activated for battery applications):**
5-15% Ash

**XRF Characterization From Ni/Bi melt**

<table>
<thead>
<tr>
<th></th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>95.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.4</td>
</tr>
<tr>
<td>Bi</td>
<td>4.3</td>
</tr>
</tbody>
</table>
“Cleaner” Carbon in Two-Phase Salt/Metal Melts

NiBi-KBr  1000 C
10 sccm CH₄ 24 hrs
Conversion: 55%

After hot water wash
+ 1000 C vacuum dist.

<table>
<thead>
<tr>
<th>Ni (wt%)</th>
<th>Bi (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10-0.51</td>
<td>0.01-0.28</td>
</tr>
</tbody>
</table>

Nazanin Rahimi
In Salts Solubilities Are Complicated

Key Issue: Understand and Control Liquid-C Interactions
Estimate Costs Based on Commercially Practiced Systems

Chem. Engin. & Tech 6, 40 (2017)
The lowest cost, 24/7 dispatchable electricity (and heat) can be produced from low cost fossil fuels without CO₂ – on demand.

PV/Wind Electricity = $0.10/kWh

Methane → Heat

Pyrolysis H₂ Combustion
Electricity = $0.05/kWh

Pyrolysis H₂ → Heat

NG price assumed $3/GJ
10 Year capitalization

Chem. Engin. & Tech
6, 40 (2017)
Vehicles that run on hydrogen are already produced: Plan B can work today!

Toyota Mirai About 500 lb lighter than a BEV

Fuel Cell Stack

Massive Impact Today

500 tons/hr coal \sim 3 \text{ GW}_{heat} \sim 1 \text{ GW}_{elec} ~ 1000 \text{ tons/hr CO}_2
Reverse the Carbon Flow
450 tons/hr NG $\sim 3\ \text{GW}_{\text{heat}}$ $\sim 1\ \text{GW}_{\text{elec}}$

$\sim 500$ tons/hr H$_2$O
Zero CO$_2$

$\sim 340$ tons/hr Solid Carbon

Use existing rail and grid infrastructure and workers!
Lowest Cost 24-7 Dispatchable CO$_2$-free Electricity
Summary: The rest of the universe runs on H₂ why don’t we?

Specific melts with high C and H solubility can shift the reaction equilibrium allowing high conversion at high P and produce solid carbon free of contamination.

Selection of the melt can influence the rates and characteristics of the carbon produced. Molten metals, salts, and suspended and fixed solid catalysts are active and can produce separable C.

Methane pyrolysis can be performed at high rates in catalytic high temperature liquid environments.
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