Mendenhall Glacier, Juneau, AK

June ‘71
Rapid climate change

Spruce bark beetle kill, Alaska
Shishmaref, Alaska
Winter storms coastal erosion
35,000 walrus have come ashore in NW Alaska: usual sea ice is gone
35,000 walrus stranded in NW Alaska: their usual sea ice is gone
Baby walruses are often crushed during stampedes ashore.
MUST Run the World on Renewables – plus Nuclear?

- Climate Change
- Ocean acidification
- Sea level rise
- Demand growth
- Water for energy
- War
- Depletion of Oil and Gas and Coal
- Only Source of Income:
  - Sunshine, tides
  - Spending our capital
Comparing the world’s energy resources*

Where should we invest for the long-haul??

Annual Income

Capital

SOLAR

World energy use

© Richard Perez, et al.

*Yearly potential is shown for the renewable energies. Total reserves are shown for the fossil and nuclear “use-them, lose-them” resources. World energy use is annual.
Running the World on Renewables: Alternatives to Electricity for Transmission and Low-cost Firming Storage of Stranded Renewables as Hydrogen and Ammonia Fuels via Underground Pipelines

ASME Energy Sustainability and Fuel Cell Science
30 June – 2 July 2014, Boston

Bill Leighty, Director
The Leighty Foundation
Juneau, AK
wleighty@earthlink.net
907-586-1426 206-719-5554 cell
Trouble with Renewables

• Diffuse, dispersed: gathering cost
• Richest are remote: “stranded”
  – High intensity
  – Large geographic extent
• Time-varying output:
  – “Intermittent”
  – “Firming” integration + storage required
• Distributed AND centralized
Trouble with Renewables: Big Three

1. Gathering and Transmission
2. Storage: Annual-scale firming → dispatchable
3. Integration
   - Extant energy systems
   - Electricity grid
   - Fuels: CHP, transportation, industry
Beyond “Smart Grid”

- Next big thing; panacea
- Primarily DSM
- More vulnerable to cyberattack?
- Adds no physical:
  - Transmission, gathering, distribution
  - Storage
- Run the world on renewables?
- Must think:
  - Beyond electricity
  - Complete energy systems
  - ALL energy
“Transmission”

- Electrofuels
  - CHP on-site: Combined Heat and Power
  - Transport
  - Industrial
- Renewable-source electricity
- Underground pipelines
- Carbon-free fuels: hydrogen, ammonia
- Low-cost storage: $0.10 – 0.20 / kWh capital
- RE systems, GW scale
Solar Hydrogen Energy System

Sunlight from local star

- Electricity
- Electrolyzer
- Fuel Cell
- Work

H₂ + O₂ → H₂O + Energy

2H₂ + O₂ → 2H₂O + Energy

www.h-tec.com
Landscape: RE-source NH3

- Alaska demo project: AASI
- Complete RE systems:
  - Generation, harvesting
  - Gathering + Transmission
  - Annual-scale firming storage
  - Integration: distribution + end-use
- Artificial Photosynthesis: UK, July ‘14
- Ag Ventures Alliance, Iowa: Wind → NH3 study
- Synthesis tech survey
  - From H2
  - From electricity
- ICE gensets conversion to NH3: demand demo
Our NFuel unit: Sustainable and decentralized production of Ammonia for usage as a fuel, fertilizer or de-nox
PROJECT: Complete RE - NH₃ Synthesis + Storage System

> NH₃ synthesis from RE electricity, water, air (N₂)
> Liquid NH₃ tank storage
> Regeneration + grid feedback
> SCADA instrumentation → UAF - ACEP
## Alaska NH3 Pilot Plant Budget

<table>
<thead>
<tr>
<th>Description</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>EETF via AEA</td>
<td>$ 750 K</td>
</tr>
<tr>
<td>Technology in-kind</td>
<td>$ 100 K</td>
</tr>
<tr>
<td>WindToGreen in-kind</td>
<td>$ 100 K</td>
</tr>
<tr>
<td>AASI in-kind</td>
<td>$  50 K</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$ 1 M</strong></td>
</tr>
</tbody>
</table>

**Abbreviations**

- **EETF**: Emerging Energy Technology Fund, State of Alaska
- **AEA**: Alaska Energy Authority, State of Alaska
- **AASI**: Alaska Applied Sciences, Inc.
Landscape Survey: RE-source NH3

- WindToGreen, LLC technology survey
- Researchers always want “Better catalysts”
- New methods, pathways, to NH3 synthesis
- All “Non-Haber” tech is at TRL 1-3
- Electrolysis + Haber-Bosch (EHB) is lowest risk
- Long-term, costly effort ahead for RE-NH3
- High cost of RE-NH3: competition, C-tax?
**Landscape: RE-source NH3**

– Sources: Electricity or Hydrogen?

– Markets:
  - Transportation Fuel
  - Ag Fuel
  - N-fertilizer
  - Distributed Generation (DG) Fuel
  - Industrial Fuel + Feedstock
  - “Run World on Renewables”
RE Systems: Carriers and Storage Strategies

- Electricity
- Gaseous Hydrogen (GH2)
- Liquid Hydrogen (LH2)
- Anhydrous Ammonia (NH3)
- Toluene (C7H8) \( \leftrightarrow \) Methylcyclohexane (C7H14)
- Artificial Photosynthesis (AP)
C-emissions-free Hydrogen transport and storage: Chiyoda Chemical, Japan
Toluene (C7H8) ↔ Methylcyclohexane (C7H14)
**RE Systems:**

**Carriers and Storage Strategies**

- Electricity
- Gaseous Hydrogen (GH2)
- Liquid Hydrogen (LH2)
- Anhydrous Ammonia (NH3)
- Toluene (C7H8) \( \leftrightarrow \) Methylcyclohexane (C7H14)
- Artificial Photosynthesis (AP)
Global Artificial Photosynthesis Project
The Royal Society, Chicheley Hall, UK  July 8 – 10, 2014
Tom Faunce, Australia National University, Convenor
Leighty for NH3 Fuel Association: “What Shall We Do With The Photohydrogen?”
**RE Ammonia Transmission + Storage Scenario**

- **Wind Generators**
- **Electrolyzers**
- **Air Separation Plant**
  - Electricity
  - Air
  - $\text{N}_2$
- **Haber-Bosch Ammonia Synthesis**
  - $\text{H}_2$
  - $\text{H}_2\text{O}$
- **Liquid Ammonia Tank Storage**
- **Liquid Ammonia Transmission Pipeline**
- **Generators**
  - ICE, CT, FC
- **AC grid Wholesale**
- **End users Retail**
  - Cars, Buses, Trucks, Trains
- **Aircraft Fuel**
Ammonia from hydrogen from zero-cost off-peak hydro
Inside the Black Box: HB Plus Electrolysis

\[ 3 \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \frac{3}{2} \text{O}_2 \]
\[ 3 \text{H}_2 + \text{N}_2 \rightarrow 2 \text{NH}_3 \]

Energy consumption \( \sim 12,000 \text{ kWh per ton NH}_3 \)
RE Ammonia Transmission + Storage Scenario

Beyond Haber-Bosch “BHB”

Wind Generators

Electrolyzers

Air Separation Plant

Air

Haber-Bosch Ammonia Synthesis

H2

H2O

Liquid Ammonia Tank Storage

Liquid Ammonia Transmission Pipeline

Generators ICE, CT, FC

AC grid Wholesale

End users Retail

Cars, Buses, Trucks, Trains

Aircraft Fuel
Wind Generators

Air Separation Unit (ASU)

N₂

SSAS reactor

H₂O

Liquid Ammonia Transmission Pipeline

Generators
ICE, CT, FC

End users
Retail

Cars, Buses, Trucks, Trains

Aircraft Fuel

AC grid Wholesale

Beyond Haber-Bosch “BHB”
“Atmospheric” Liquid Ammonia Storage Tank (corn belt)

30,000 Tons
190 GWh
$15M turnkey
$80 / MWh
$0.08 / kWh

-33 C
1 Atm

'09 ARPA-E “Grids” Goal: $100 / kWh
NH3 Synthesis Technologies

- WindToGreen, LLC, 2013
- Technology Advisory Group
- Landscape assessment
- Literature search
- Personal followup with researchers
NH3 Synthesis Technologies

- Haber-Bosch (H-B) and electrolysis plus H-B (EHB)
- Polymer membrane: nano as enabling technology
  - Nanoparticle catalyst impregnated polymer membrane
  - Nanostructure catalyst
  - Nanostructured polymer membrane
  - Other nanoparticles catalysts and nanostructure catalyst carriers
  - Composite electrolytes
- Polymer membrane “Nafion”: not compatible with NH3
- Ammonia-Compatible Polymer (UMinnesota): Marc Hillmyer’s Nanostructured PEM, alleged to be durable in NH3
- Membrane Electrode Assembly (MEA): PEM fuel cell
NH3 Synthesis Technologies

- Proton Conducting Ceramic (PCC) electrolytes:
  Examples (BaCeO3, CaZrO3, SrZrO3, LaGaO3)
- Other PCC: MP2O7 Intermediate-temp PCC + M-N catalysts at Los Alamos National Lab (LANL)
- Oxides:
  • Complex perovskite-type
  • Pyrochlore-type
  • Fluorite-type
- Oxygen ion conducting ceramic electrolyte
- Plasma
  • Non Thermal (NTP)
  • Microwave
Beyond Haber-Bosch "BHB"

Emulate SOFC construction
NH3 Synthesis Technologies

- Molten salt electrolyte
  - Licht
  - Hyung Chool Yoon
- Ionic Liquid electrolyte
- Diamond nanoparticles catalyst, substrate, deep UV light: U. Wisconsin Madison (R.J. Hamers)
- Solar-assisted two-stage metal nitride redox, low-P NH3 synth, from ETH, Zurich
- N2 Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex
- Cyclic Pressurization (ICE)
- Lithium (proprietary)
H2 generation to feed H-B

- Artificial Photosynthesis (AP)
- Catalyst pseudo-random search: JCAP
- Biology: algae, other
- Gasification
- Nanoptek, proprietary:
  light or electricity input → H2
- Other
**TLR TRL Levels and Definitions**

- **TRL 1**: Basic principles observed and reported
- **TRL 2**: Technology concept and/or application formulated
- **TRL 3**: Analytical and experimental critical function and/or characteristic proof of concept
- **TRL 4**: Technology basic validation in a laboratory environment
- **TRL 5**: Prototype demonstration in a relevant environment
- **TRL 6**: Technology prototype demonstration in a simulated operational environment
- **TRL 7**: Actual Technology completed and qualified through test and demonstration
- **TRL 8**: Actual Technology qualified through successful mission operations
- **TRL 9**: System Test, Launch & Operations
Electrolysis + Haber-Bosch (EHB) system
For RE-source Electricity, Water, and Air inputs
Review of electrochemical ammonia production technologies and materials

S. Giddey, S.P.S. Badwal, A. Kulkarni

CSIRO Energy Technology
Victoria, Australia
Fig. 2 – Various electrolytic options under consideration for ammonia synthesis.
NH₃ Synthesis by Proton Conducting Solid Electrolyte
NH3 Synthesis by Molten Salt Electrolyte
NH₃ Synthesis via Molten Salt Electrolyte
With Water as Hydrogen Source
Proton Conducting Ceramic Electrolyte Cell

**TOP:** Double-chamber

\[ 6H^+ + N_2 + 6e^- = 2NH_3 \]

**Anode**
\[ H_2 = 2H^+ + 2e^- \]

**Cathode**

**BOTTOM:** Single-chamber

\[ 6H^+ + N_2 + 6e^- = 2NH_3 \]
\[ 3H_2 + N_2 = 2NH_3 \]

**Anode**
\[ H_2 = 2H^+ + 2e^- \]
Cluster Model of “NAFION” Membrane

\[ \sim 10^{-8} \text{ mol per cm}^2 \text{ per second} \]
What is NTP?

NTP species include: energetic electrons, photons, atoms, and molecules, highly reactive radicals, ozone, etc. Ozone is the most widely used NTP species.

NTP is generated through electrical discharge in gas (in atmosphere or liquid).

Highest single-pass conversion = 13%

Source: Roger Ruan, University of Minnesota
Solar Thermochemical Ammonia
P. Pfromm, R. Michalsky*, Kansas State University

On tower: fixed bed reactor, manganese

Solar tower with heliostats

Reaction chamber
Concentrated solar radiation

Ammonia

Manganese nitride

700°C

1000-1250°C

Reaction chamber

Steam
Manganese oxide

N2
from membrane air separation unit

*N2, O2

*now ETH, Zurich
Plasmon-Induced Ammonia Synthesis through Nitrogen Photofixation with Visible Light Irradiation
Ag Ventures Alliance, Mason City, Iowa
Electrolysis + Haber-Bosch (EHB) system
For RE-source Electricity, Water, and Air inputs
Our NFuel unit: Sustainable and decentralized production of Ammonia for usage as a fuel, fertilizer or de-nox

Proton Ventures BV, Netherlands
www.protonventures.com
Figure III

Ammonia Prices
(Average, New Orleans)

Source: Green Markets

Source: FINDS, Keith Stokes
Figure II
Ammonia Prices
(Average, New Orleans)

Source: Green Markets

Source: FINDS, Keith Stokes
Figure V
Regional Nitrogen Price Premium Over U.S. Gulf (NOLA) Price ($U.S./metric tonne)

Case A-1: Self-generate Wind

Total Annual Cost of NH3

Capital Recovery Factor (CRF) per cent

Capital Recovery

BOS Purch Elec Energy

O&M Except Elec Energy
Case A-1: Self-generate Wind

Cost of NH3 per Mt (Metric ton) at plant gate

*Capital Recovery Factor (CRF) per cent*
### Case A-2: Self-generate Wind; no Grid Connect

The chart above illustrates the total annual cost of NH3 production as a function of the Capital Recovery Factor (CRF) per cent in a self-generate wind scenario without grid connection. The cost breakdown includes capital recovery, BOS (Balance of System) purchase of electric energy, and O&M (Operations and Maintenance) except for electric energy. The graph shows an increasing trend in total annual cost with higher CRF values. The chart is color-coded to differentiate between capital recovery, BOS purchase of electric energy, and O&M except for electric energy.
Case A-2: Self-generate Wind; no Grid Connect

Cost of NH3 per Mt (Metric ton) at plant gate

Capital Recovery Factor (CRF) per cent

- 8%
- 10%
- 12%
- 14%
- 16%
- 18%

$0.00
$200.00
$400.00
$600.00
$800.00
$1,000.00
$1,200.00

Cost of NH3 per Mt (Metric ton) at plant gate
Case A-4: Self-generate Wind: High Wind AEP

The graph shows the Total Annual Cost of NH3 for different Capital Recovery Factor (CRF) percentages. The cost is broken down into Capital Recovery, BOS Purch Elec Energy, and O&M Except Elec Energy. The CRF percentages are 8%, 10%, 12%, 14%, 16%, and 18%. The costs increase as the CRF percentage increases, with the highest cost at 18% CRF.
Case A-4: Self-generate Wind: High Wind AEP

Capital Recovery Factor (CRF) per cent

Cost of NH3 per Mt (Metric ton) at plant gate
Case B-1: Buy Wind @ $0.05 / kWh

Total Annual Cost of NH3

Capital Recovery Factor (CRF) per cent

- **Capital Recovery**
- **Buy wind**
- **BOS utility electricity**
- **O&M non-energy**
Case B-1: Buy Wind @ $0.05 / kWh

Cost of NH3 per Mt (metric ton) at plant gate
Case B-3: Buy Wind @ $0.05 / kWh; High Capital Cost EHB

Total Annual Cost of NH3

Capital Recovery Factor (CRF) per cent

- Capital Recovery
- Buy wind
- BOS utility electricity
- O&M non-energy

Year: 8, 10, 12, 14, 16, 18

Costs: $0, $100,000, $200,000, $300,000, $400,000, $500,000, $600,000, $700,000, $800,000
Case B-3: Buy Wind @ $0.05 / kWh; High Capital Cost EHB

Cost of NH3 per Mt at plant gate

- 8 Mt: $600.00
- 10 Mt: $700.00
- 12 Mt: $800.00
- 14 Mt: $900.00
- 16 Mt: $900.00
- 18 Mt: $900.00
Conclusion

Landscape: RE-source NH3

- Alaska demo project: AASI
- Artificial Photosynthesis: UK, July ‘14
- Ag Ventures, Iowa: Wind → NH3 study
- Synthesis tech survey
  - From H2
  - From electricity
- ICE gensets conversion: demand demonstrate
- Complete RE-source energy systems
Conclusion
Landscape: RE-source NH3 Synthesis

1. H-B reactor only good candidate
   - RE - H2 + N2
   - RE electricity $\rightarrow$ electrolyzer $\rightarrow$ H2 + O2
   - Complex system: suited for Alaska deployment?
   - MWe input scale costs, efficiency unknown

2. Beyond Haber-Bosch “BHB” Electrolytic
   - Diverse technologies
   - TRL 1 – 3
   - Less complex system than H-B and EHB?
   - MWe input scale costs, efficiency unknown
Conclusion

Landscape: RE-source NH3 Synthesis

• Electricity source RE:
  H-B reactor only good candidate
  Electrolysis plus Haber-Bosch (EHB)
• Hydrogen source RE:
  H-B reactor only good candidate
  Beyond Haber-Bosch “BHB” Electrolytic
• Many technology options:
  All TRL 1 – 3
  Years and $ for R&D, Demo, to commercialize
NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling

DVD’s + Handouts

Ammonia Fuel Association
21 – 24 September 2014
Des Moines, Iowa  USA

Bill Leighty, Director
The Leighty Foundation
Juneau, AK
wleighty@earthlink.net
907-586-1426       206-719-5554 cell