NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling

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

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Mendenhall Glacier, Juneau, AK

June ‘71
Mendenhall Glacier, Juneau, AK
10 October 10
Rapid climate change

Spruce bark beetle kill, Alaska
Shishmaref, Alaska
Winter storms coastal erosion
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
  - Spreading 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. Word 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

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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 $\rightarrow$ 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
- Electrolyzer
- Fuel Cell
- Work
- Electricity
- $H_2$
- $O_2$

Reaction:

$2H_2O + \text{Energy} \rightarrow 2H_2 + O_2$

$2H_2 + O_2 \rightarrow 2H_2O + \text{Energy}$
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, 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

Proton Ventures BV, Netherlands
www.protonventures.com
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
# Pilot Plant Budget

<table>
<thead>
<tr>
<th>Project</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 tech survey
- “Better catalysts”
- New methods, pathways, to NH3 synth
- All “Non-Haber” tech is at TRL 1-3
- Electrolysis + Haber-Bosch (EHB) lowest risk
- Long-term, costly effort 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)
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?”
Chicheley Hall, The Royal Society, UK
RE Ammonia Transmission + Storage Scenario

- Wind Generators
- Electrolyzers
- Air Separation Plant
- Haber-Bosch Ammonia Synthesis
- Liquid Ammonia Tank Storage
- Liquid Ammonia Transmission Pipeline
- Generators (ICE, CT, FC)
- Cars, Buses, Trucks, Trains
- AC grid Wholesale
- End users Retail
- Aircraft Fuel

Electricity

Air

N\textsubscript{2}

H\textsubscript{2}

H\textsubscript{2}\textsubscript{0}
Norsk Hydro
Electrolyzers
2 MW each

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 ~12,000 kWh per ton NH$_3$
**RE Ammonia Transmission + Storage Scenario**

Beyond Haber-Bosch “BHB”

Wind Generators → Electrolyzers

Air Separation Plant

N₂ → Haber-Bosch Ammonia Synthesis

H₂ → Liquid Ammonia Synthesis

H₂O → Liquid Ammonia Tank Storage

Liquid Ammonia Transmission + Storage

Electricity → Air

Generators ICE, CT, FC

Cars, Buses, Trucks, Trains

Aircraft Fuel

End users Retail

AC grid Wholesale

**Diagram Elements:**
- Wind Generators
- Electrolyzers
- Air Separation Plant
- Haber-Bosch Ammonia Synthesis
- Liquid Ammonia Tank Storage
- Liquid Ammonia Transmission
- Generators ICE, CT, FC
- Cars, Buses, Trucks, Trains
- Aircraft Fuel
- Electricity
- Air
- N₂
- H₂
- H₂O
Beyond Haber-Bosch “BHB”
C-emissions-free Hydrogen transport and storage: Chiyoda Chemical, Japan
Toluene (C7H8) ↔ Methylcyclohexane (C7H14)
NH3 Synthesis Technologies

- WindToGreen, LLC  2013
  Technology Advisory Group
- Landscape assessment
- Literature search
- Followup
NH3 Synthesis Technologies

- H-B and electrolysis plus H-B (EHB)
- Polymer membrane: nano
  - 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 (UMN)
- 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 (LANL)
- Oxides:
  • Complex perovskite-type
  • Pyrochlore-type
  • Fluorite-type
- Oxygen ion conducting ceramic electrolyte
- Plasma
  • Non Thermal (NTP)
  • Microwave
Beyond Haber-Bosch “BHB”
NH3 Synthesis Technologies

- Molten salt electrolyte
- Ionic Liquid electrolyte
- Diamond nanoparticles catalyst, substrate: 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: light or electricity input $\rightarrow$ H2
- Other
**Technology Readiness Level (TRL)**

- **TRL 9**: Actual Technology qualified through successful mission operations
- **TRL 8**: Actual Technology completed and qualified through test and demonstration
- **TRL 7**: Technology prototype demonstration in a simulated operational environment
- **TRL 6**: Prototype demonstration in a relevant environment
- **TRL 5**: Technology basic validation in a relevant environment
- **TRL 4**: Technology basic validation in a laboratory environment
- **TRL 3**: Analytical and experimental critical function and/or characteristic proof of concept
- **TRL 2**: Technology concept and/or application formulated
- **TRL 1**: Basic principles observed and reported
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

- \[ \text{Cathode: } \text{N}_2 + 6e^- = 2\text{N}^{3-} \]
- \[ \text{LiCl-KCl-CsCl + Li}_3\text{N} \downarrow \text{N}^{3-} \text{ Electrolyte} \]
- \[ \text{Anode: } 2\text{N}^{3-} + 3\text{H}_2 = 2\text{NH}_3 + 6e^- \]
- \[ 2\text{N}^{3-} = \text{N}_2 + 6e^- \]
- \[ \text{N}_2 + \text{H}_2 + \text{NH}_3 \]
NH₃ Synthesis via Molten Salt Electrolyte With Water as Hydrogen Source
Proton Conducting Ceramic Electrolyte Cell

TOP: Double-chamber

BOTTOM: Single-chamber

(a) $6\text{H}^+ + \text{N}_2 + 6\text{e}^- = 2\text{NH}_3$

H$_2$ = 2H$^+$ + 2e$^-$

(b) $6\text{H}^+ + \text{N}_2 + 6\text{e}^- = 2\text{NH}_3$

3H$_2$ + N$_2$ = 2NH$_3$

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%
Solar Thermochemical Ammonia

P. Pfommm, R. Michalsky*, Kansas State University

*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 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)


Source: FINDS, Keith Stokes
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

NH₃ cost per Mt at plant gate

Capital Recovery Factor (CRF) per cent

Cost of NH₃ per Mt (Metric ton) at plant gate
Case A-2: Self-generate Wind; no Grid Connect

Capital Recovery Factor (CRF) per cent

<table>
<thead>
<tr>
<th>CRF per cent</th>
<th>Total Annual Cost of NH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>$400,000</td>
</tr>
<tr>
<td>10</td>
<td>$500,000</td>
</tr>
<tr>
<td>12</td>
<td>$600,000</td>
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<tr>
<td>14</td>
<td>$700,000</td>
</tr>
<tr>
<td>16</td>
<td>$800,000</td>
</tr>
<tr>
<td>18</td>
<td>$900,000</td>
</tr>
</tbody>
</table>

- Capital Recovery
- BOS Purch Elec Energy
- O&M Except Elec 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

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

Total Annual Cost of NH3

Capital Recovery Factor (CRF) per cent

- Capital Recovery
- BOS Purch Elec Energy
- O&M Except Elec Energy
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

- 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 at plant gate

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

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

Cost of NH3 per Mt 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

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

Capital Recovery | Buy wind | BOS utility electricity | O&M non-energy
Case B-3: Buy Wind @ $0.05 / kWh; High Capital Cost EHB

The chart shows the cost of NH3 per Mt (metric ton) at plant gate for different years. The costs range from $600.00 to $900.00. The costs increase over time, indicating higher costs as the years progress.
**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 demo
- Complete RE-source energy systems
Landscape: RE-source NH3 Synthesis

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

2. Beyond Haber-Bosch “BHB” Electrolytic
   - Diverse technologies
   - TRL 1 – 3
   - Less complex system?
   - MWe input scale costs, efficiency unknown
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, Commercialize
NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling

DVD’s + Handouts

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