Power-to-Gas

Biomethanation: A Unique and Sustainable Approach to Renewable Natural Gas and other products

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National Renewable Energy Laboratory

AGA/EPA 2019 Renewable Natural Gas Workshop

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Advanced energy technologies are providing real-world solutions by:

- Becoming increasingly cost-competitive
- Boosting the U.S. energy industry
- Providing jobs for American workers

Costs for Renewables are Falling

Recent U.S. Electricity “New Capacity”

Far from “alternative,” renewable energy and natural gas is the new normal in the United States.
Figure 4. Total Renewable Generation Serving California Load by Resource Type

Source: California Energy Commission, staff analysis November 2018
H₂@Scale Initiative

Benefits of Renewable H₂
- Enables higher penetration of renewable electricity
- Electrolyzer can provide grid services
- H₂ provides flexibility
- O₂ is a byproduct, too
- Growing transportation sector

Reduces fossil fuel consumption Scaleable, non-toxic, low temperature process

10 MM tons H₂/year in U.S.
https://www.energy.gov/eere/fuelcells/h2scale
Storing Renewable Electricity as Molecules

Electricity, transportation, feedstock and heat
- NG has high energy density ~7x greater than H₂
- Existing national energy transmission system
- Flexibility in energy use
- Shifting RE with seasonal energy storage
- High scalability of P2G and RNG Production

Over 130 billion cubic feet of natural gas storage capacity exists in Southern California.

To put this in perspective, this is enough to supply all of the gas-fired generation in the region for more than two months.

- SoCalGas
Wind and Solar Curtailment Totals

Solar and wind curtailed by year
- Production only assume: 50 kWh/kg H₂
- Thru August of 2019 alone, over 76,000 Metric Tons of CO₂ could have been recycled!
Waste-to-Energy: Biogas Sources of CO₂

End Uses: Heat, fuel, chemical feedstock

Meets SoCalGas’ Rule 30 gas quality standard

HHV R30: 970-1150
CO₂ R30: 3% max
H₂ R30: 0.1%

Trigger* *SoCalGas does not have a shut-off limit, but this level triggers additional study/testing.
Renewable Hydrogen Production

Step 1: Using renewable electricity to split water into hydrogen and oxygen in an electrolyzer

\[ \frac{1}{2} \text{H}_2 \text{O} + e^- \rightarrow \text{H}_2 + \text{O}_2 + \text{Heat} \]

Rules of Thumb
- MW-scale: 50 - 55 kWh make 1 kg of H\(_2\)
- 1 MW\(_e\) electrolyzer, ~400 kg /day
- 1 kg H\(_2\) ~1 gallon of gasoline (gge)

\( \frac{1}{2} \)" dia. H\(_2\) tube at 400 psig
Electrolyzer systems are flexible electrical loads that can help stabilize the electrical grid and enable higher penetrations of renewable electricity.

**Supporting grid stability**
- Typical utility profile to validate performance
- System response, not just stack
- 120 kW PEM stack operating on NREL’s electrolyzer stack test bed
- Flexible demand side management tool could be used to provide frequency response service

Source: Harrison K., Mann M., Terlip D., and Peters M., NREL/FS-5600-54658
**Biomethanation - RNG Production from CO₂**

**Step 2:** Using the renewable H₂ (from Step 1) and CO₂ in a downstream biomethanation process to produce renewable methane and water

\[ 4H₂ + CO₂ \xrightarrow{\text{Biocatalyst}} CH₄ + 2H₂O + \text{Heat} \]

**Benefits of Biomethanation**

- Recycles CO₂ .... As well as the CH₄
  - Ethanol, dairies, wastewater, breweries, fossil
- Meets (SoCalGas’) pipeline quality standards
  - 998 BTU/CF, 0.89% CO₂, 0.4% H₂
- Scale-able, non-toxic, self-replicating biocatalyst,
- Low temperature (65°C) systems

**Rule of Thumb:** 10MWₑ of electrolysis feeding a bioreactor can produce ~500 scfm (12,000 Nm³ or 440 MMBTU per day/6 g/L-hr) of methane and recycles ~20 tons of CO₂ per day
H₂ & RNG Systems at NREL

Electrolyzer System
- Today, 250 kW PEM stack
  - 5 kg H₂ / hr
- 30 bar H₂ Pressure
  - Up to 70 bar max
- (4) Power Supplies
  - Current-sharing mode
  - 4000 A dc at 250 V dc

H₂ and RNG R&D Site
#1) 350 and 700 bar pre-cooled H₂ dispensing system
#2) Diaphragm and piston compressors
#3) 700 L bioreactor - operates at 18 bar (260 psig) and 60 - 65°C with agitation, recirculation loop and cell recycle
#4) 200, 400 & 900 bar storage - 350 kg Total
Varying Input Gas Flows

- **Step-up and step-down response shown**
- **Bioreactor can load follow like an electrolyzer**
- **Challenge:** Low density gas, like H₂, is difficult to monitor

**Goal:** Maintain > 98% methane production under varying input gas flows
- Trace CO₂, H₂ and H₂S remaining
- **Maintain H:C Ratio**
  - Ideally 4:1 H₂ to CO₂
SoCalGas – 700L Bioreactor Start-up

After 24 hours of total operation conversion reached 92%

- During this start-up phase the biocatalyst grew to 10x the initial population
- Agitation reached 50% of maximum RPM
- Flow rates 20% of rated
- Reactor pressure 4 bar during this time
  - 18 bar (260 psig) max.

Percentage (%)

Low Agitation
- 0.6 kg/hr H2
- 3.0 kg/hr CO2

Increased Agitation
- Started new Day at lower agitation

Methane

CO2

Day 1 Day 2 Day 3 Day 4

Hours of Operation

0 5 10 15 20 25
Increasing Pressure to Improve Conversion

Conversion reached 98%

Conversion = \( \frac{\% \text{ CH}_4}{\% \text{ CH}_4 + \% \text{ CO}_2} \)

Operational State
- Start pressure 5 bar
- Returned to low agitation rate
- 0.6 kg/hr H\text{\textsubscript{2}}
- 3.0 kg/hr CO\text{\textsubscript{2}}

Graph showing:
- Increased pressure to 6 Bar
- Increased pressure to 7 Bar
- Increased agitation 50%

Percentage (%) vs. Hours of Operation
- % Conversion
- Methane
- CO\text{\textsubscript{2}}
**Biocatalyst - Methanogenic Archaea**

**Growth Requirements**
- Seawater environment
- Salts and minerals
- 60 – 65°C
- Anaerobic conditions
- Feedgas: CO₂ and H₂

**Long Term Stability**
- Capable of daily startup
- “Load” following
- Robust
- Self-replicating
- Fast recovery during start/stop cycles

**Methanothermobacter thermautotrophicus**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td><strong>Efficient</strong></td>
<td>98.6% of carbon goes into methane</td>
</tr>
<tr>
<td><strong>Productive</strong></td>
<td>VVD* of 800, H₂ mass-transfer limited</td>
</tr>
<tr>
<td><strong>Responsive</strong></td>
<td>Quick return to methane production within seconds/minutes</td>
</tr>
<tr>
<td><strong>Selective</strong></td>
<td>100% methane, no intermediates</td>
</tr>
<tr>
<td><strong>Robust</strong></td>
<td>Tolerant to oxygen, H₂S, CO, Sulfate, Ammonia, particulates</td>
</tr>
<tr>
<td><strong>Simple</strong></td>
<td>Moderate temperature range (60 – 65°C)</td>
</tr>
</tbody>
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Electrochaea’s proprietary biocatalyst is a selectively evolved - not genetically modified - strain of *methanogenic archaea*, a single-celled microorganism that has populated Earth for billions of years.

http://www.electrochaea.com/technology/
Challenge - Reducing the Cost of H₂
Upcoming Projects

- DOE Bioenergy Technology Office, SoCalGas and Electrochaea
  - **Biopower:** Upgrade biogas to pipeline quality RNG
  - Design and build a scaled-down mobile bioreactor
  - Analytical development

- SoCalGas, Bioenergy and Fuel Cell Technology Offices
  - **H2@Scale:** Systems integration and optimization
  - IP development
  - Gas mixing and mass transfer
Biomethanation - Bulk Energy Storage and...

- Recycles CO₂ in addition to the CH₄
- Sector Coupling - Electrons-to-Molecules
- Biogas and pure CO₂ are potential sources
- Uses the existing NG network (2.5 Million miles)
- Produces a “Drop-in” replacement for fossil NG
- Heat and oxygen are (also) produced in this two-step process
- Enables higher penetrations of solar- and wind-generated electricity

- Shifts, in time and space, the production of renewable electricity

Meets SoCalGas’ Rule 30 gas quality standard

Higher Heating Value: R30: 970-1150
BTU/CF Carbon Dioxide: 3% max.
Hydrogen: R30 - 0.1% Trigger for more testing and study, SoCalGas does not have a shut off limit set.
Pictures taken on August 13, 2019 at NREL’s 3rd Partnership Forum during the SoCalGas bioreactor dedication ceremony
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System Comparison

<table>
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<tr>
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<th>P2G - BioCat</th>
<th>P2G - SoCalGas</th>
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<tbody>
<tr>
<td>Location</td>
<td>Copenhagen, DK</td>
<td>NREL - Golden, CO</td>
</tr>
<tr>
<td>Volume</td>
<td>3,500 L</td>
<td>700 L</td>
</tr>
<tr>
<td>Electrolyzer</td>
<td>1 MW - Alkaline</td>
<td>125 kW - PEM</td>
</tr>
<tr>
<td>Production</td>
<td>30.4 scfm CH₄</td>
<td>4.1 scfm CH₄</td>
</tr>
<tr>
<td>CO₂ Source</td>
<td>Avedøre WWTP</td>
<td>Delivered</td>
</tr>
<tr>
<td>Pressure</td>
<td>9 bar</td>
<td>18 bar</td>
</tr>
</tbody>
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“The core of our power-to-gas system is a selectively evolved microorganism – a methanogenic archaea – that excels through unprecedented catalytic ability and industrial robustness.”

http://www.electrochaea.com/about/
### Scientific Approach

- Utilize excess electricity production for the electrolysis of water to $\text{H}_2$ and $\text{O}_2$
- Optimized strain of methanogenic archaea to perform methanation under industrial conditions
- 98% Carbon efficiency of $\text{CO}_2$ to $\text{CH}_4$
- Post-processing for pipeline quality natural gas

### Significance and Impact

- Potential long term storage strategy via conversion of electricity & $\text{CO}_2$ to $\text{CH}_4$
- High efficiency $\text{CO}_2$ capture and conversion strategy
- Demonstrated route to renewable methane

### BioCat Project

**Power-to-gas - biological catalysis**

- **1) Electrolyzer**
- **2) Pre-Processing**
- **3) BioCat Reactor**
- **4) Post-Processing**

**Chemical Reaction:**

$$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} + \text{Heat}$$