# HyBrTec, Renewable Hydrogen from Wastewater and Biosolids


**POC**
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# Technical Background

- Chemergy's HyBrTec wet-biowaste-to-hydrogen process exploits efficient thermo- and electro-chemistry in two steps:
  - First, biosolids and wastewater (biowaste) are thermochemically processed to produce a weakly bonded intermediate hydrogen carrier
  - Secondly, the hydrogen carrier is electrochemically dissociated to recover the hydrogen content of both biosolid and water feedstocks
- Along with low-cost renewable hydrogen HyBrTec co-produces
  - 175$^{o}$ C heat
  - Potable water
  - Can co-provide an energy storage capability

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# Recovering Hydrogen from Biowaste

- Burning dried biowaste with air ($O_2$) produces heat, water ($H_2O$) and carbon dioxide ($CO_2$).
  - $C_6H_{10}O_5 + 6O_2 \rightarrow 5H_2O + 6CO_2$ + thermal energy
  - $H_2O$ is a strongly-bonded hydrogen carrier

- HyBrTec ‘burns’ biowaste (biosolids and wastewater) with bromine ($Br_2$) producing heat, hydrogen bromide (HBr) and $CO_2$
  - $C_6H_{10}O_5 + 7H_2O + 12Br2 \rightarrow 24HBr + 6CO_2$ + thermal energy
  - HBr is a weakly-bonded hydrogen carrier
- HBr and unreacted water form hydrobromic acid ($HBr_{aq}$)
- The $HBr_{aq}$ is electrolyzed recovering the hydrogen content of the feedstock and recyclable bromine reagent
  - $2HBr_{aq} \rightarrow H_2 + Br_2$

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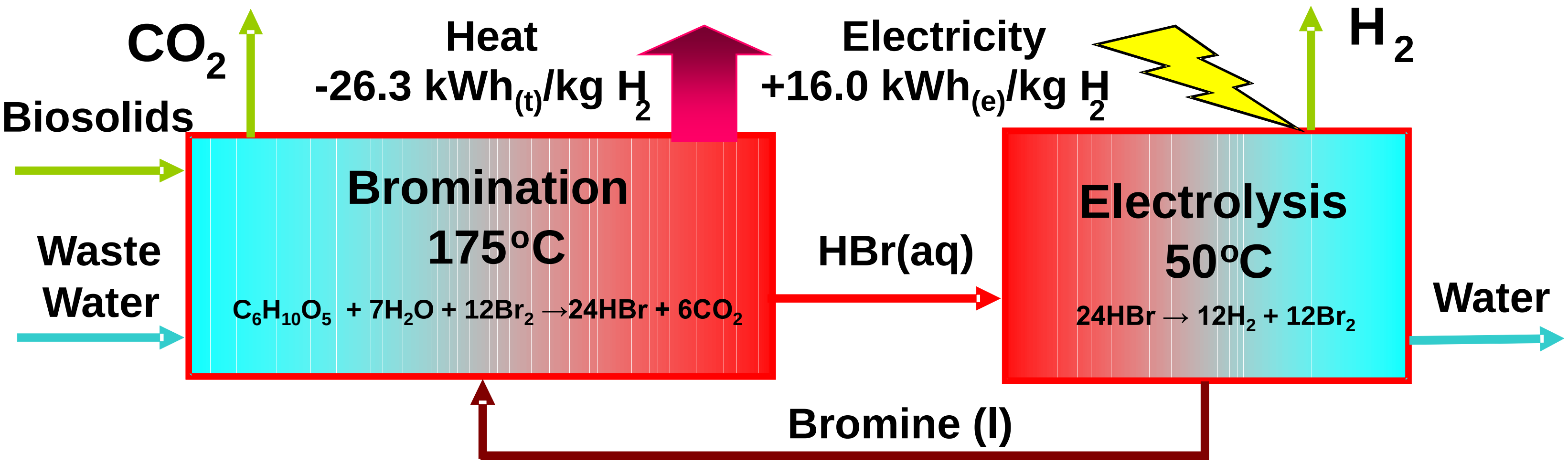
# HyBrTec's Thermo-electrochemistry




- **Bromination:** $C_6H_{10}O_5 + 7H_2O + 12Br_2 \rightarrow 24HBr + 6CO_2$
- **Electrolysis:** $24HBr \rightarrow 12H_2 + 12Br_2$
- **Overall:** $C_6H_{10}O_5 + 7H_2O \rightarrow 12H_2 + 6CO_2$
- **Net enthalpy change:** -10.3 kWh/kg $H_2$
  - 58% of recovered hydrogen is from wastewater
  - 4-6 gallons of fresh water is co-produced per kilo of hydrogen due to electroosmotic transfer

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# Electroosmotic Water Production

Hydrogen bromide electrolyzers use proton exchange membrane (PEM) cells. In these cells, hydrogen ions (protons) cross the PEM, pick-up an electron at the cathode, and evolve as hydrogen. This exchange process causes water transport to occur due to electroosmotic transfer from the bromine anode to the hydrogen evolution cathode.

The water transport is desirable as it increases the hydrobromic acid concentration at the anode, lowering cell voltage, and results in pure water at the cathode.

The number of water molecules transported depends on the PEM properties, but typically 4-6 water molecules per proton, producing 4-6 gallons of potable water with each kilo of hydrogen.*

****Fundamentals of Energy Processes***, Aldo Viera da Rosa, 2005

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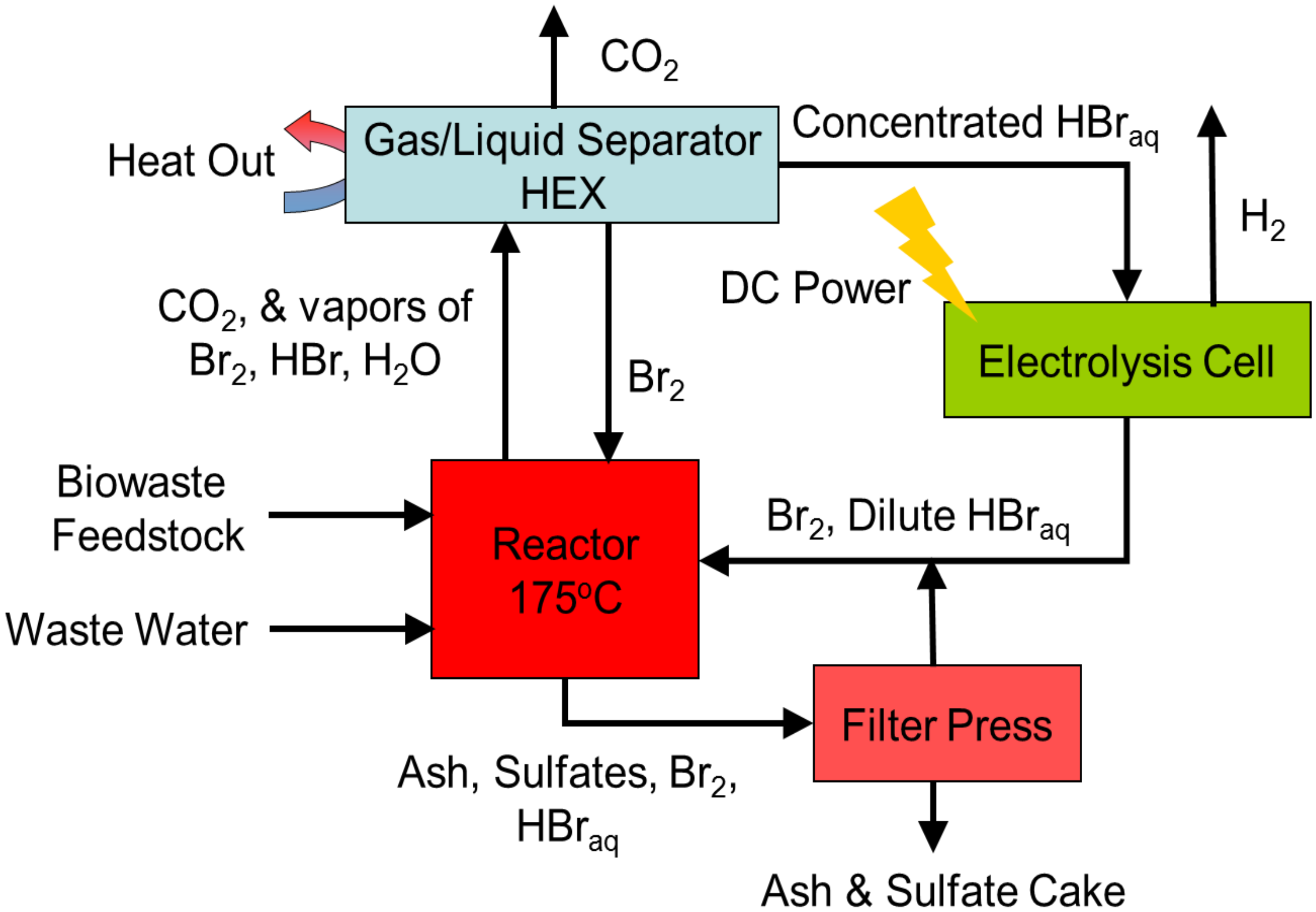
# Process Flow

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# Benefits of HBr Electrolysis

"…the hydrogen bromide (HBr) cycle looks the most promising because of its wider operating window (i.e., large current densities), lower cell voltage, less expensive catalyst ($RuO_2$) rather than Pt), and more stable operation."[1]

[1] *IV.I.3 Low Temperature Electrolytic Hydrogen Production,* SRNL Contract #: DE-FC36-04GO14232, DOE Hydrogen Program, FY 2005 Progress Report

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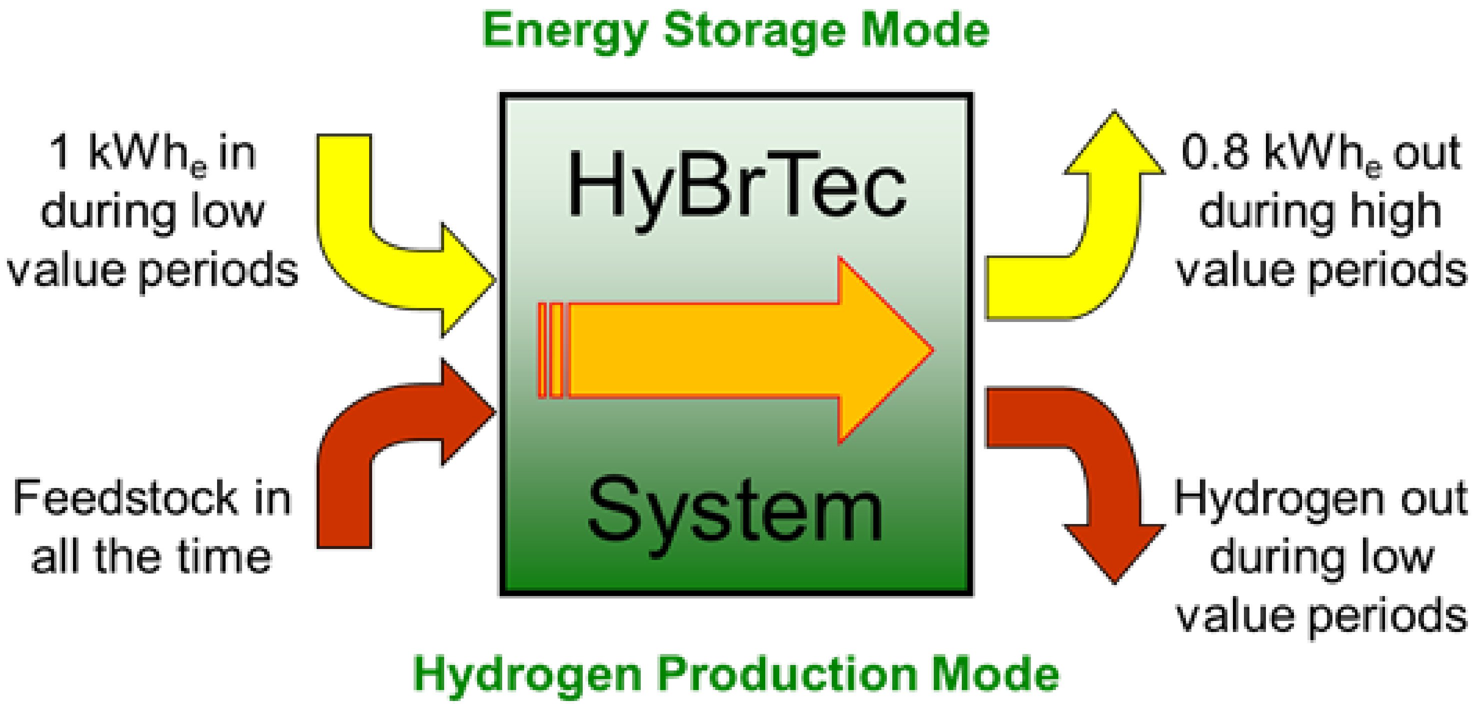
# HBr-based Energy Storage

- HBr electrochemistry is reversible ($2HBr \leftrightarrow H_2 + Br_2$)
- Can co-provide $H_2$ production and energy storage
  - Charging: electrolyze HBr into $H_2$ and $Br_2$
    - Converts electricity into storable chemical energy
  - Discharging: produce electricity as a fuel cell
    - Converts stored chemical energy into electricity by recombining $H_2$ and $Br_2$.

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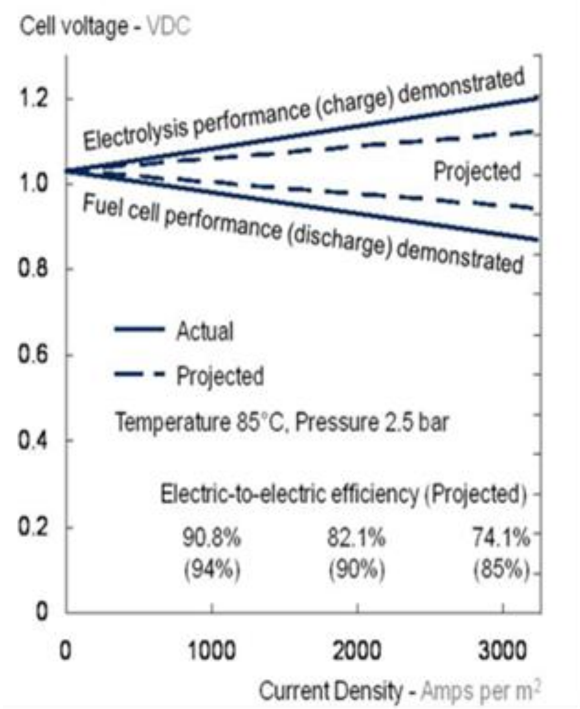
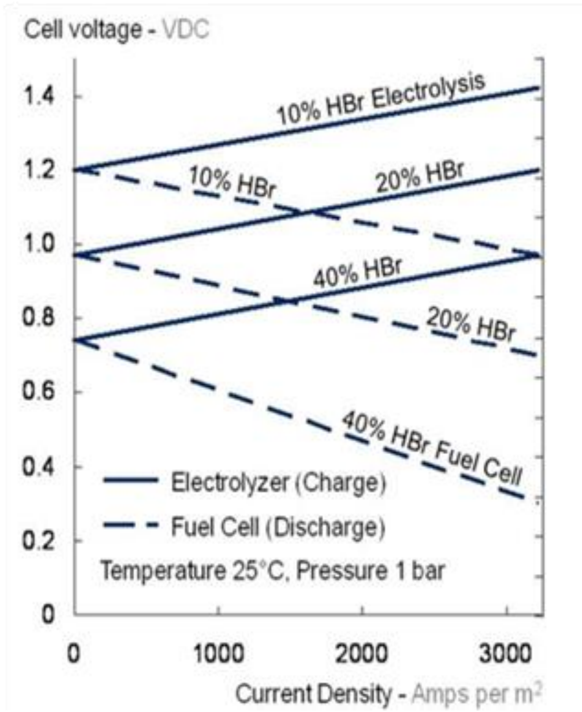
# $H_2$-$Br_2$ Energy Storage Efficiency

- The charge vs. discharge voltages below show electric-to-electric efficiencies greater than 100% could be possible
  - maintain a high (40%) concentration by adding HBr from bromination during electrolysis to keep a low (<1V) charging voltage
  - during the fuel cell cycle adding water to have a low HBr concentration (10%) will keep a high (>1V) discharge voltage.

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# Safety

- Bromine, like chlorine is a halogen; however, it is much less corrosive and toxic than chlorine and as a liquid easier to use
  - Toxicity (Pauling Units): $Br_2$ (2.96) < $Cl_2$ (3.16) < $F_2$ (3.98)
  - Safety follows that of the chlor-alkali industry that in the U.S. produces over 11.5 million tons of chlorine annually without incident
  - Incorporates primary and secondary features including:
    - All reagents are in solution with water
    - Small quantity of $Br_2$ continuously recycled
    - Highly reliable UL approved equipment and material
    - Safety factors of 50% rather than 10%
    - Active monitors to detect incipient failure
    - Built-in passive neutralization of any leakage
    - $Br_2$ is neutralized with soda ash, NaOH & KOH
    - $HBr_{aq}$ is neutralized with limestone into benign NaBr

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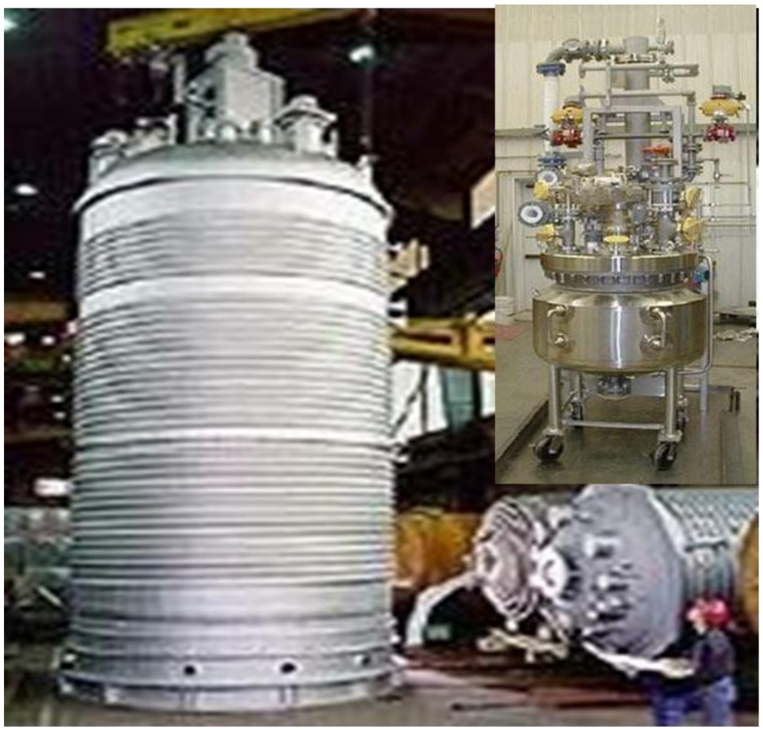
# Primary Systems

- All components are commercially available at any scale
  - Glass-lined reactors are well-established in chemical processing
  - Electrolysis cells are from the chlor-alkali industry for producing chlorine



- Glass-lined reactor
  - 5 to 20,000 gallon
- Electrolysis system
  - kW to MW

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# Technology Development

- Development programs:
  - In 2010 under the auspices of the U.S. DOE and the Florida Hydrogen Initiative experiments with cellulose were successful
  - In 2013 the California Energy Commission (CEC) funded to:
    - Determine suitability of sewage biosolids from the Delta Diablo WWTP
    - Prepare a system design and cost estimate of a pilot system
    - Forecast a financial analysis of a commercial system
  - In 2020 the Florida Department of Environmental Protection (FDEP) has approved funding a pilot system processing sewage biosolids
    - In response to waterways contamination due to nutriment overloading
    - Teamed with Miami Dade Water and Sewer Department (MDWASD)

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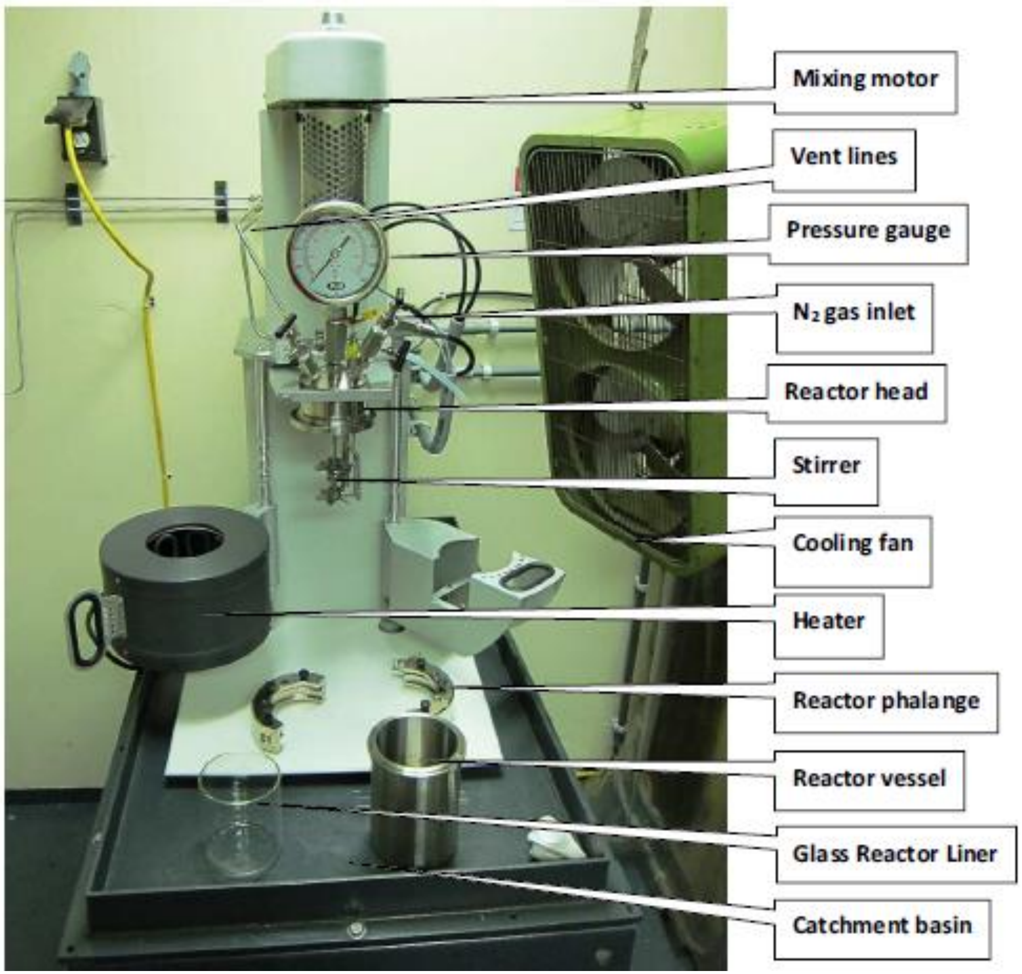
# Reactor Lab for CEC Program

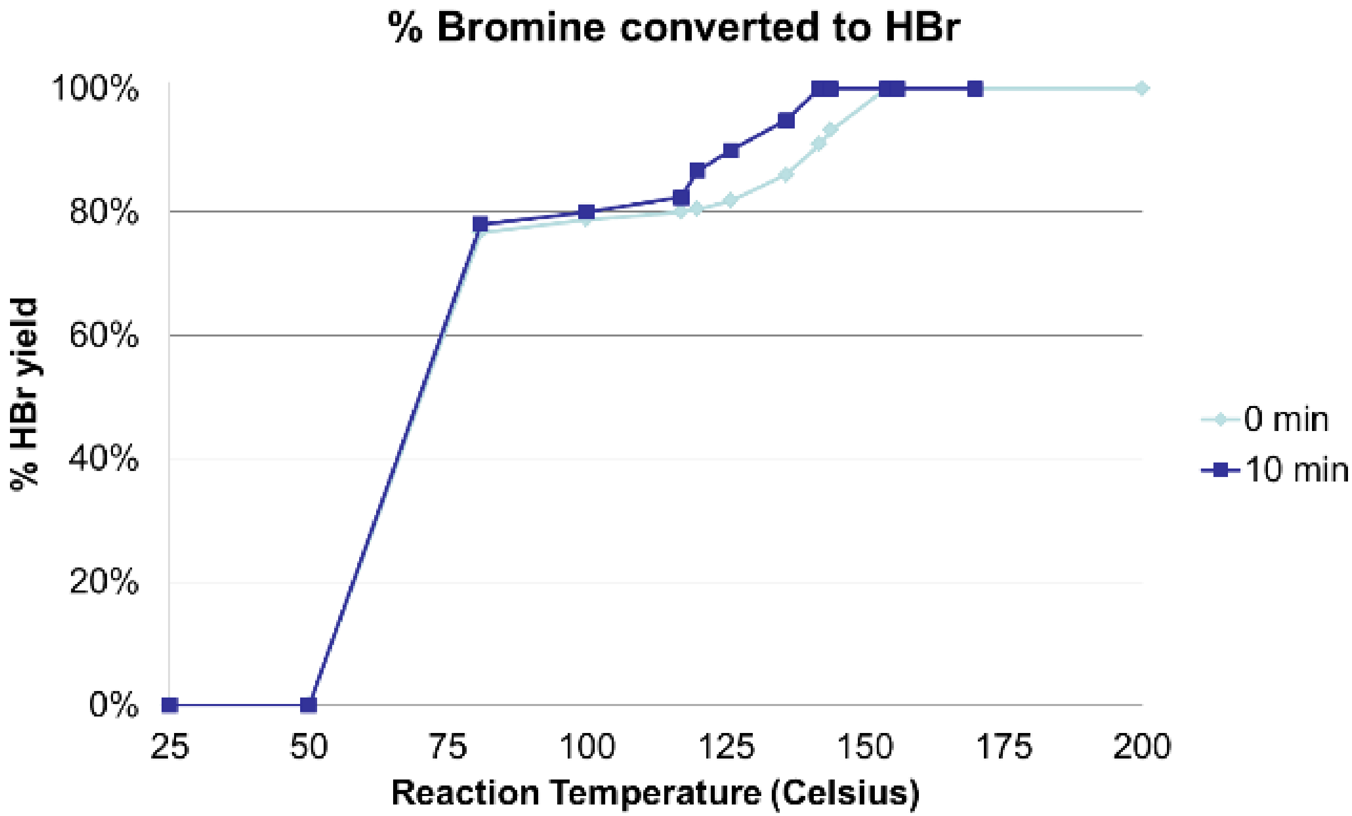
# Bromination Reactor




**Setup allows investigation to 300 Celsius and 3000 psi**

# Bromination Results

Conversion of $Br_2$ and feedstock to HBr and $CO_2$ at 120 psi & 150° C [1]



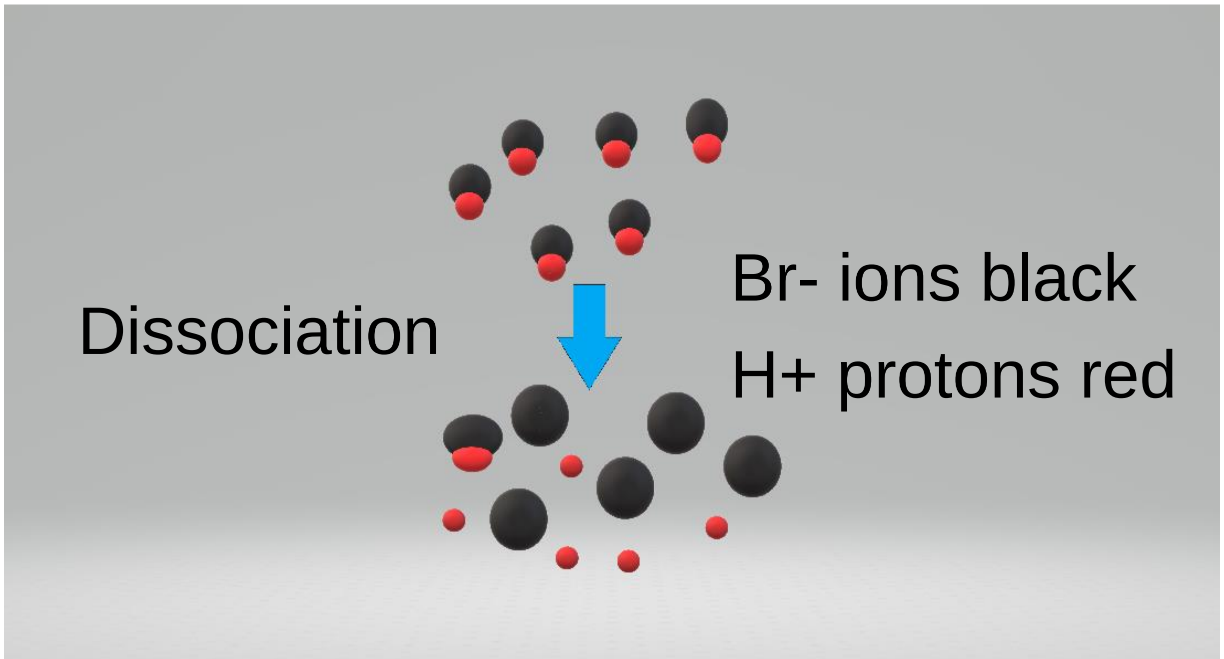

Reaction time at set temperature[2]

[1] 100% conversion of $Br_2$ to HBr; no brominated carbonaceous species.

[2] Reaction time does not include ~10 mins to ramp temp up and ~5 mins to quench

# Hydrobromic Acid ($HBr_{aq}$)

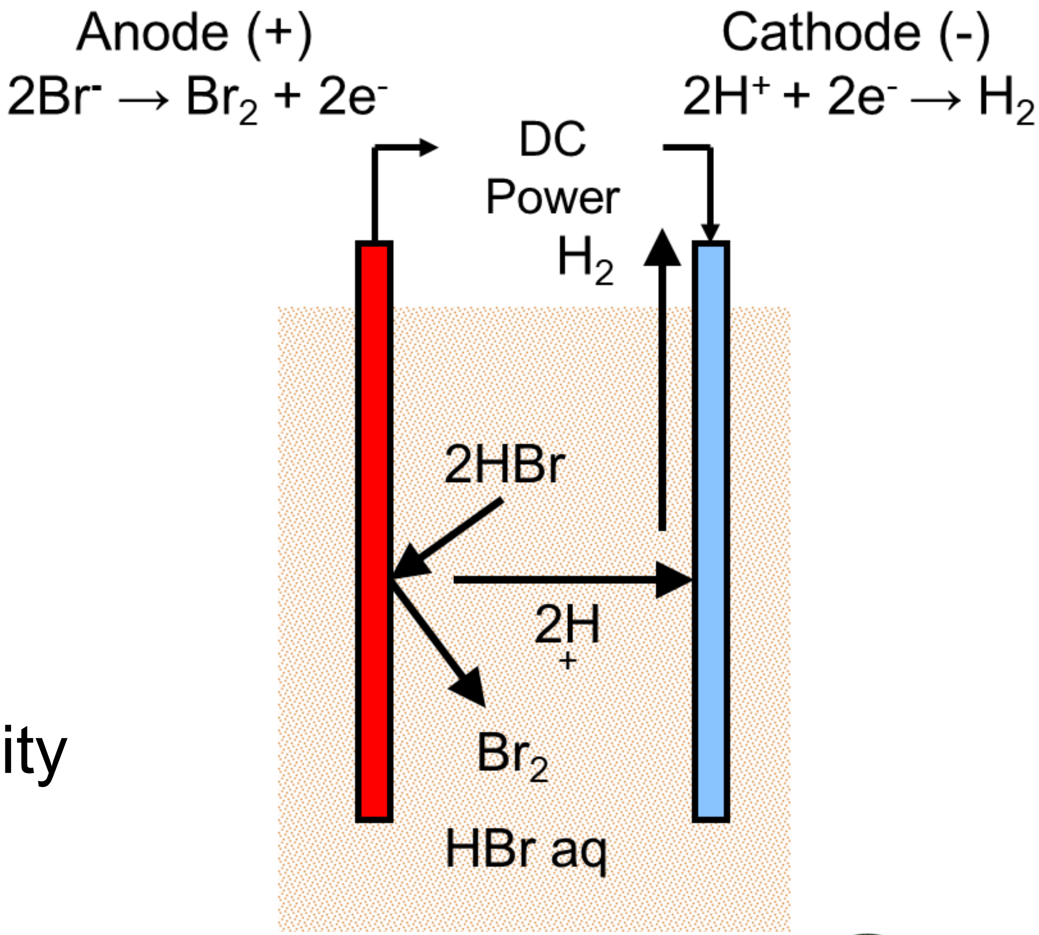
- $HBr_{aq}$ is a strong acid because the overlap of orbitals between the H and Br atom is small due to the different 1s and 4p orbital size, hence the bond strength of H-Br is weak and is easily broken. Also, the Br- ion is a relatively stable ion because its negative charge is diffused over the large orbital size of 4p orbitals, reducing charge density, so the dissociation constant (pKa) for HBr will be high (-8.8 ± 0.8).



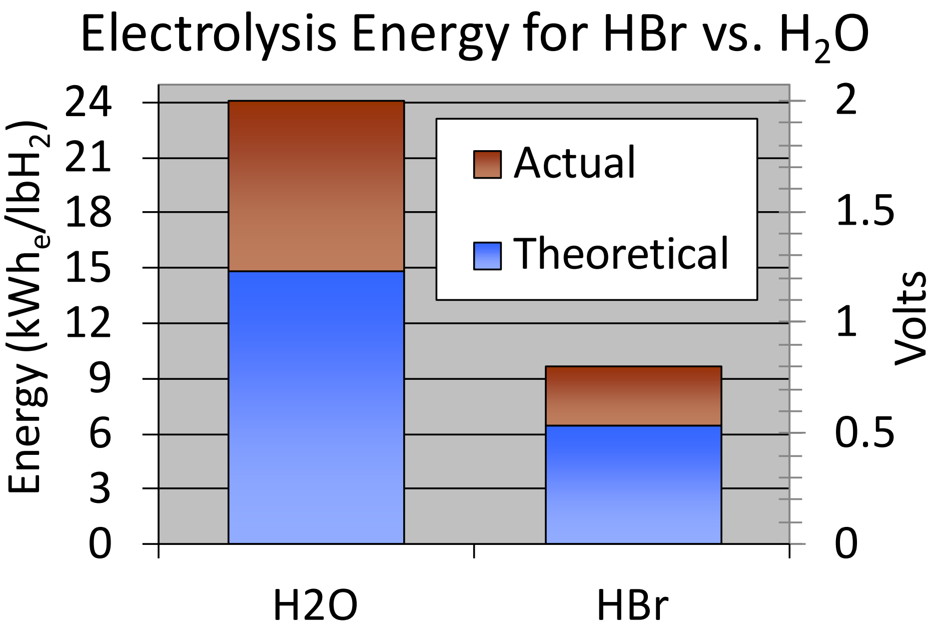
# Second step: $HBr_{aq}$ Electrolysis

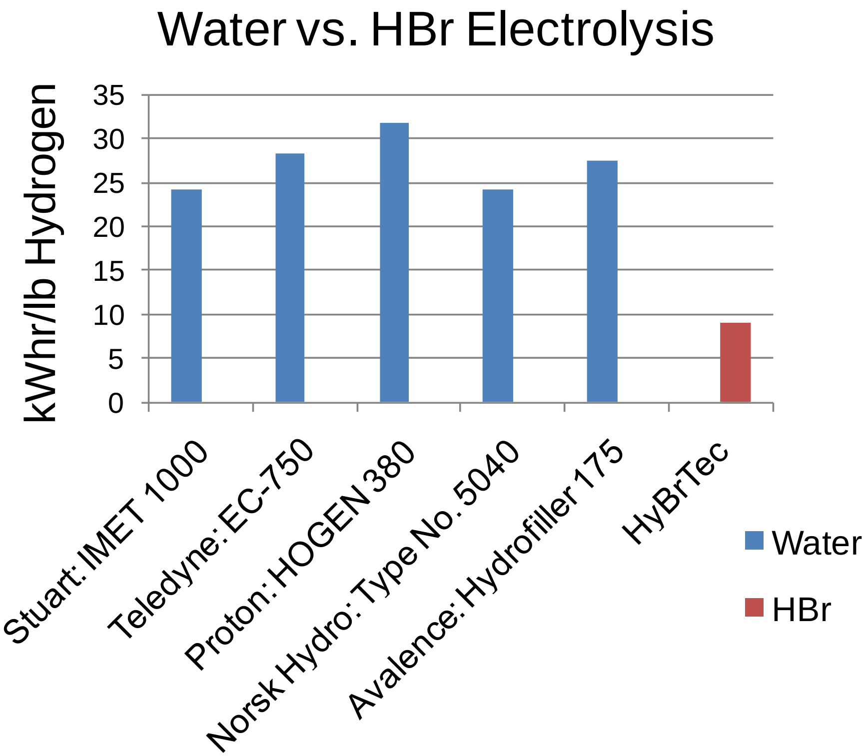
- $2HBr_{aq} \rightarrow H_2 + Br_2$
  - Endothermic
  - <1.0 Volt at 50ºC
  - 16-18 $kWh_{elec}/kg\ H_2$
  - 85% elec. efficiency

- $Br_2 \rightarrow$ recycled
- $H_2 \rightarrow$ fuel or electricity



# $HBr_{aq}$ Electrolysis vs. $H_2O$ Electrolysis




- $H_2O$ electrolysis requires pure pre-treated water
- HBr electrolysis improves with conductive contaminates in the electrolyte

***Summary of Electrolytic Hydrogen Production (Water Electrolysis)***, September 2004, NREL/MP-560-36734

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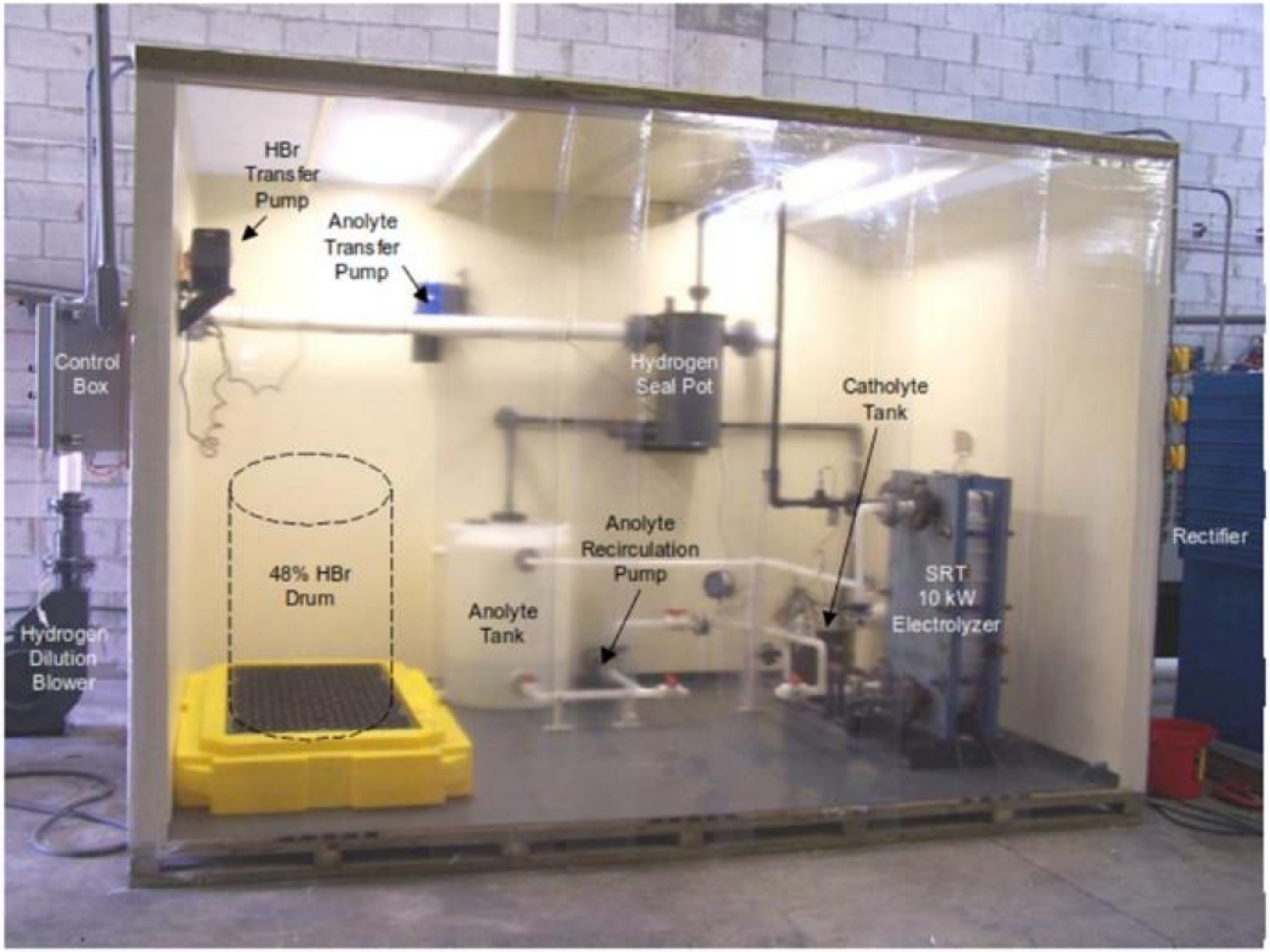
# Electrolysis Lab for CEC Program

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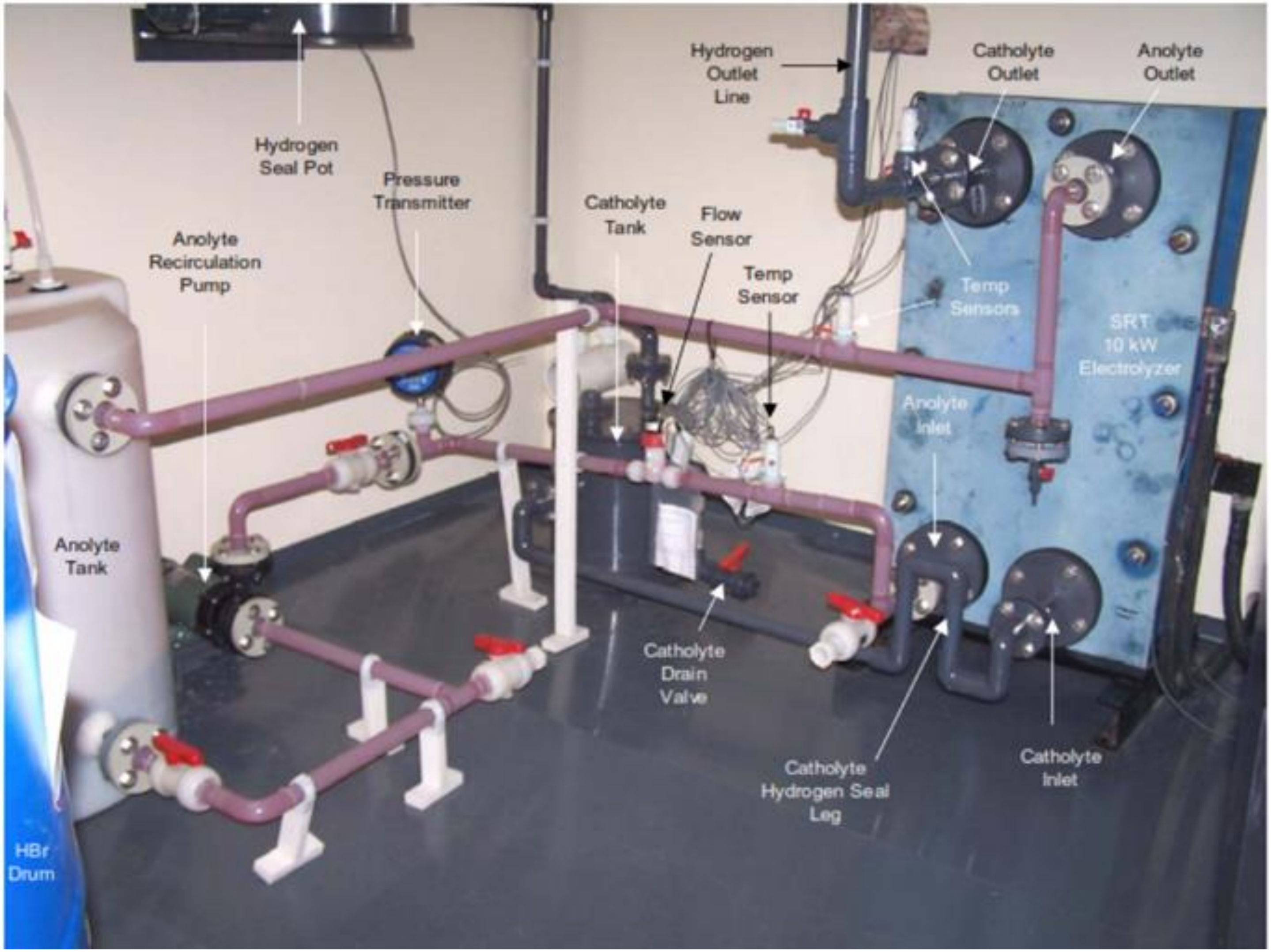
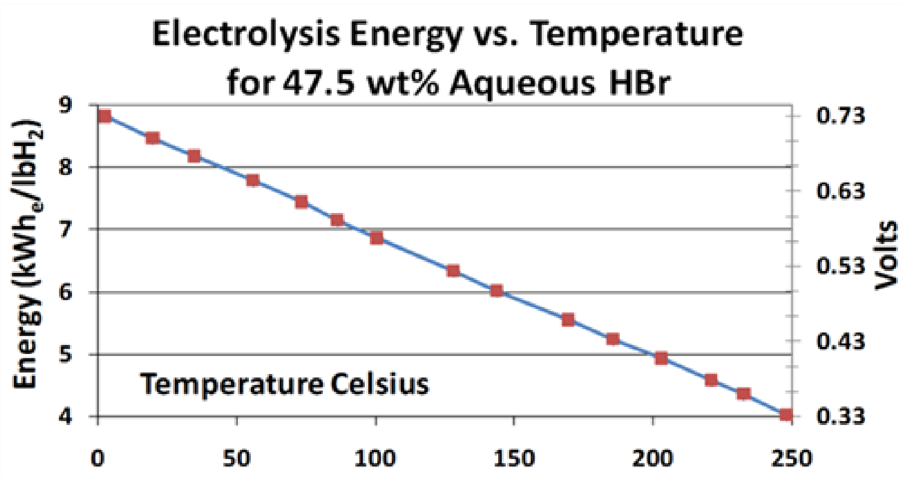
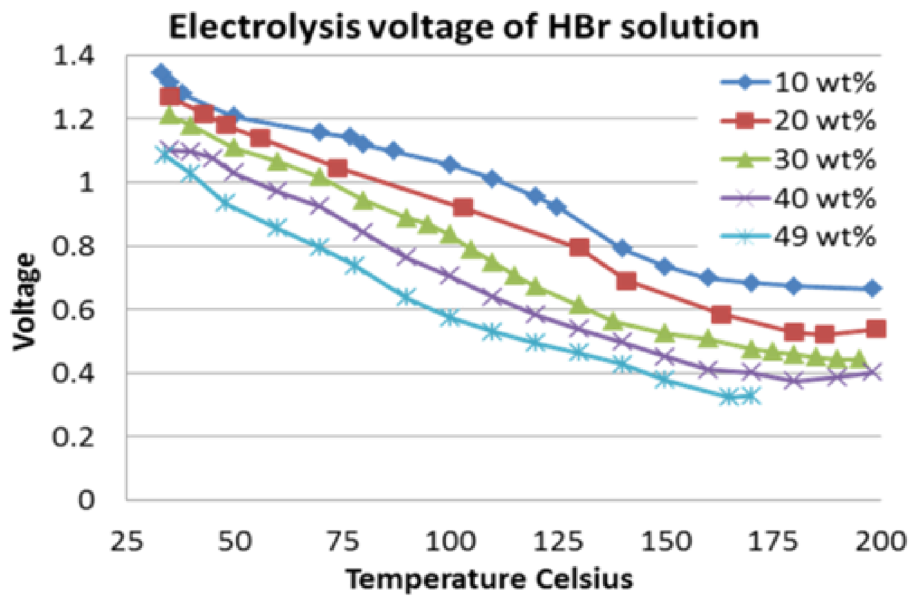
# Electrolysis Stack



# Electrolysis Results

- The bond strength of H-Br is weak and is easily broken.
- Energy required is temperature and concentration dependent




- Allowing reduced voltages at elevated temperatures and concentrations, which can be achieved using the bromination thermal energy to heat and concentrate the electrolyte.

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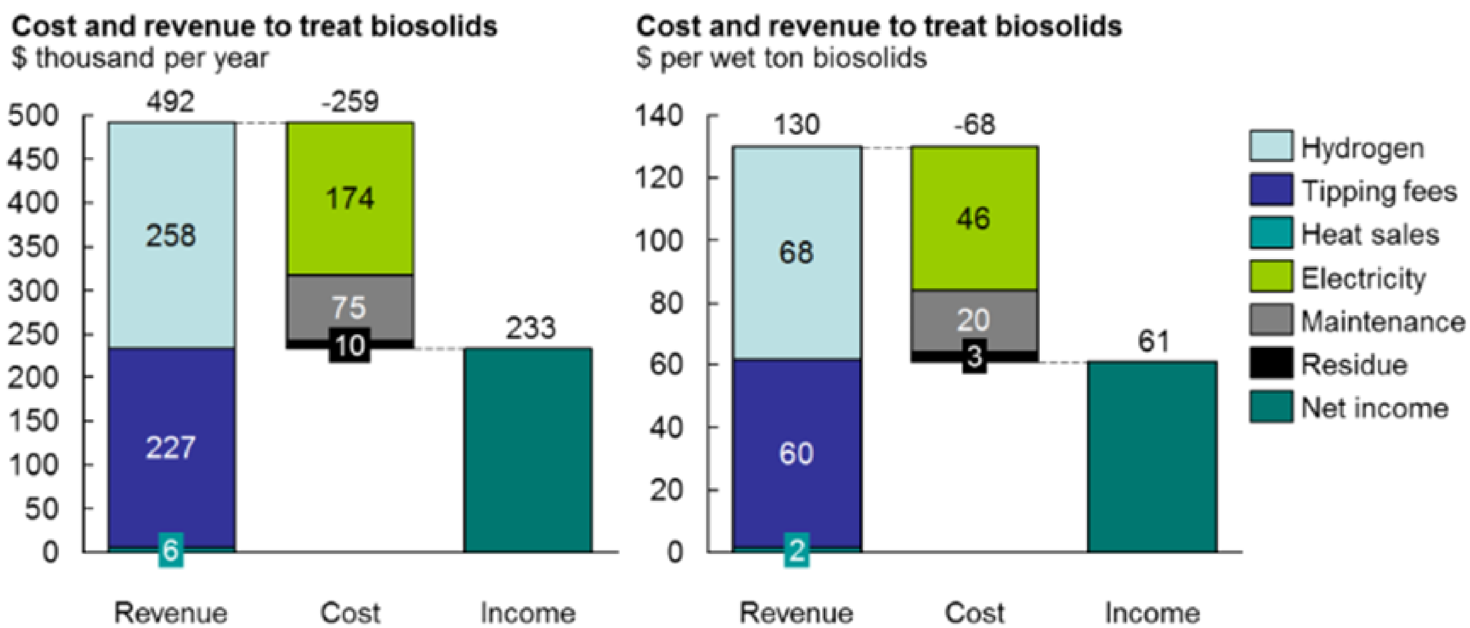
# CEC Economic Projections

- Alpha prototype analysis assumed
  - $3/kg price for hydrogen
  - $1.5 million capex
  - 11.4 wet-ton of sewage sludge
  - 236 kg of hydrogen daily
- Analysis predicted
  - 14% internal rate of return
  - 6.4 years simple payback
  - $1,168,000 net present value over 20 years @ 6% discount

Energy storage, state & federal incentives, loan guarantees, cap & trade credits and subsidies were not included in the financial analysis.



# CEC Program Results Summary

- The R&D program was successful with the following results:
  - Reaction between bromine and sewage-biosolids occurs readily
  - Hydrobromic acid, carbon dioxide and heat are reaction by-products
  - Hydrobromic acid was electrolyzed at room temperature at <1 Volt
  - 100 kg of hydrogen can be recovered from 4 wet-ton (1 dry-ton) of sewage biosolids
  - Feedstock wet-mass is reduced by 95%
  - $2/kg of hydrogen recovery cost promises favorable economics

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# FDEP Program Background

- 300 Florida wastewater treatment plants (WWTP) landfill 65,500 dry tons of sewage biosolids annually
- Biosolid nutriments pollute waterways and promote algae growth
- The toxic algae blooms contaminate water resources
- impacting Florida’s seafood, recreation and tourist economies

# Miami Dade Water and Sewer Department

- In 2007 Florida legislation gave the waters of South Florida special protection by banning the landfilling of biosolids
- Since then Miami-Dade Water and Sewer Department (MDWASD) has trucked north over 90,000 dry-tons of biosolids
- MDWASD produces over 100 dry-tons of biosolids daily

- MDWASD sewage finds its way into St. Johns River to ‘Devastating Effect’

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# FDEP and MDWASD Program

- MDWASD teamed with Chemergy and submitted a proposal to the FDEP to demonstrate processing sewage biosolids
- FDEP approved a 2-year $2.3 million pilot demonstration
  - $2M to Chemergy engineer, procure, construct, test and evaluate a pilot system
  - $3K to MDWASD to provide site and program support
- Based on the CEC program, Chemergy anticipates recovering 100 kg of hydrogen at a cost of $2/kg from a dry-ton of biosolids
- A successful pilot would enable Chemergy to process the 65,500 tons currently landfilled into 6,550,000 kg of hydrogen

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# Florida 2020 Clean Waterways Act

- In response to the toxic algae blooms, the Act has provisions to minimize pollution including:
- The FDEP will ensure funds are available for disposal infrastructure improvements to prevent contamination
- And to prevent discharges due to power outages from WWTP

- *Chemergy's HyBrTec will eliminate algae bloom contamination by processing biosolids into low-cost hydrogen fuel*
- *And can co-provide a WWTP with an energy storage capability that will mediate power disruptions*

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# Wastewater to Pure Water

$HBr_{aq}$ electrolysis uses proton exchange membrane (PEM) cells where H+ protons cross the PEM, get an electron at the cathode, producing $H_2$. This causes water transport due to electroosmotic transfer through the PEM to the cathode. Typically 5 water molecules transfer per proton, producing ~5 gallons of water per kg of $H_2$. This water transfer results in pure water at the cathode that carries away the evolving $H_2$.[1]

With HyBrTec, 6.75 kg of biosolids and 5.25 kg (~1.4 gal) of wastewater will provide 1 kg of $H_2$. Thus, the combined $H_2$ content of the biosolids *and* the wastewater along with ~5 gal of pure water from electroosmotic transfer are co-produced at the cell's cathode.

In addition, reacting 1 kg of $H_2$ with 8 kg of $O_2$ in air produces 9 kg or ~2.4 gal of water. Hence, ~7.4 gal of water per kilo of $H_2$ is a by-product of HyBrTec, first when producing $H_2$ and then as its emission when it's used as a fuel.

[1]*Fundamentals of Energy Processes*, Aldo Viera da Rosa, 2005

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# HyBrTec vs. Gasoline (cost of fuel)

- Hydrogen from biowaste:
  - Wet-biowaste + $Br_2 \rightarrow$ HBr
    - -26 $kWh_{th}$/kg $H_2$
  - 2HBr $\rightarrow H_2 + Br_2$
    - +16 $kWh_{elec}$/kg $H_2$
- Cost: \$.80/kg $H_2$ in electricity (\$.05/$kWh_{elec}$)

- Gasoline's price:
  - 60% crude oil
  - 13% refinery cost
  - 12% distribution
  - 16% taxes
- Cost: \$1.80/gallon in crude oil (\$3.00/gal)

- Hydrogen fuel cell is ~50% efficient ∴ from an \$.80 cost in electricity for a kilo of hydrogen, ~\$.40 provides work with a loss of ~\$.40 in electricity
- Gasoline fueled ICE is ~20% efficient ∴ from a \$1.80 cost in oil for a gallon of gasoline ~\$.36 provides work with a loss of ~\$1.44 in crude oil
- Renewable hydrogen does not have the 'well-to-wheels' environmental & health issues of gasoline
- 143 billion gallons of gasoline costing ~\$257 billion in crude oil could be replaced with ~72 billion gge of $H_2$ produced from wet-biowaste for ~\$61 billion in renewable electricity

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# Hydrogen from Dairy Cow Manure

- A producing (lactating) 600 kg dairy cow will produce ~75 kg of biowaste daily comprised of:
  - ~88% or ~66 kg of liquid waste
  - ~12% or ~9 kg of biosolids
- Providing ~3 dry-ton of biosolids annually per cow
- A dairy of 5,000 cows will produce ~15,000 dry-tons per year
- Which, it is anticipated that HyBrTec can process into:
  - ~1,500,000 kilos of hydrogen
  - ~ 135 billion Btu 175$^{o}$ C heat
  - ~225 tons of nitrogen (0.5%), phosphorous (0.5%) & potassium (0.5%)
  - ~ 7,500,000 gal of potable water
- Chemergy's estimated production cost is $2/kg, which with a wholesale price of $3/kg provides a 25-30% IRR
- Hydrogen's 2020-25 price is projected to be $8-10/kg (NREL)

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# Processing Dairy Cow Manure

- HyBrTec can recover hydrogen ($H_2$) from cow manure with 88% water content by reacting it with bromine ($Br_2$), to produce hydrobromic acid ($HBr_{aq}$), carbon dioxide ($CO_2$) and 175$^o$ C heat
  - Cow manure + bromine → hydrobromic acid + carbon dioxide
- The $HBr_{aq}$ is dissociated to recover recycled $Br_2$ reagent and $H_2$
  - $2HBr_{aq}$ (49 wt% @ 50$^o$ C) → $H_2$ + $Br_2$ $\Delta G$ = +16 $kWh_e$/kg $H_2$ (0.9V)
- The $H_2$ can be reacted with oxygen ($O_2$) to produce electricity
  - $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta G$ = -16 $kWh_e$/kg $H_2$ (50% eff. fuel cell @ 0.6V)
- Affording a theoretical round-trip efficiency approaching 100%
- Elemental nutriments (N, P, K) are recovered as a fertilizer ash
- Heat from bromination can be use for sterilization/pasteurization

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