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# **Reducing Fossil Fuel Use**

After going into overtime, the UN COP27 agreement fails to call for a †phasedown' of fossil fuels. However, Chemergy is developing economically and environmentally viable alternatives to fossil fuels, which can reduce their use.

The attached briefly describes how Chemergy's HyBrTec technology will addresses the clean hydrogen and GHG abatement goals of the President's 2022 Inflation Reduction Act, and meet the DOE 1.1.1. Moonshot Challenge.

In addition, the technology affords an efficient electrical energy storage capability that will improve the economics of intermittent renewable energy resources and promote the development of well-distributed community smart- and micro-grids.

Our pilot system recovering green hydrogen from sewage sludge for Miami-Dade County will be operational and on display in March 2023. Please put this on your calendar for a visit to Miami.

Additional submitted attachment is included below.



HOW TO ACHIEVE THE DOE MOONSHOT CHALLENGE BY RECOVERING AND RECYCLING HYDROGEN FROM WASTE AND ELIMINATING THE ECONOMIC BURDEN AND ENVIRONMENTAL LIABILITY OF ITS DISPOSAL

#### ABSTRACT

President Biden's 2022 Inflation Reduction Act affords a tremendous opportunity to wean the country off fossilfuels and create new employment opportunities, which will mitigate climate change and its impact on society. Like President Kennedy's challenge to NASA to put an American on the moon within a decade, the "Act" empowers the Department of Energy's Moonshot 1.1.1 challenge to make 1 kg of green hydrogen for \$1 within 1 decade. The following describes Chemergy's patented HyBrTec technology for accomplishing the DOE goal within years AND eliminate bio- and sulfurous-waste issues. Also, the technology can co-provide an energy storage capability that will promote the development of renewable energy resources and afford the benefits of distributed micro-grids.



### Meeting DOE's Hydrogen 1.1.1 "Moonshot" Goal

**Introduction:** In 2005 the U.S. Department of Energy's (DOE) Savannah River National Laboratory investigated and evaluated different electrolytic hydrogen production technologies. The Laboratory reported in its FY 2005 Hydrogen Program Progress Report: *Low Temperature Electrolytic Hydrogen Production*, SRNL Contract #: DE-FC36-04GO14232, the following:

"...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<sub>2</sub> rather than Pt, and more stable operation."

Question: Where can we get hydrogen-bromide?

Answer: From biosolids, organic carbonaceous waste and industrial sulfurous waste!

Over two decades ago, SRT and the DOE investigated producing hydrogen-bromide from water and bromine using solar energy: <u>https://www.youtube.com/watch?v=G2I4cmpPSI0</u>. Today Chemergy uses bio- and sulfurous-waste to do the same.

In 2020 the U.S. produced over a billion wet-tons of organic biowaste. The majority of this waste is an economic and environmental burden that requires processing and disposal at a cost of \$40-200/ton. As below, depending on its inorganic solid ash and water content, one ton of dry organic biowaste typically contains between 150-180 kilograms of green hydrogen (~50 kg/ton for wet 30wt% solids as typically received).



A kilo of hydrogen contains the Btu equivalent of one gallon of gasoline. A billion tons of U.S. biowaste, contains 50 billion kilos of green hydrogen, with the energy equivalent of 50 billion gallons of gasoline. In contrast to today's 25% efficient vehicles, this amount of hydrogen can displace 100 billion gallons of gasoline and diesel using 50% efficient hydrogen/oxygen fuel cell powered electric-vehicles. Recovering green hydrogen from biowaste eliminates fossil fuels' 'well-to-wheels' and biowastes' economic, health and environmental issues.

As a hydrogen production and waste disposal technology, Chemergy promotes a shift away from:

- 1. Non-renewable resources to environmentally harmful and negative-valued wastes.
- 2. Large central plants to small distributed and mass-produced systems.
- 3. Collecting and transporting waste feedstock to using it onsite where produced.
- 4. Centralized electric grid to distributed community microgrids
- 5. Climate changing fuels to climate neutral hydrogen.

#### THEMERGY

**The Technology:** The value of hydrogen as an emerging clean fuel is now being recognized. And, water as a renewable source is becoming accepted by stakeholders in spite of its \$3-6/kg price due to the cost of excess electricity required in its electrolysis. Chemergy's patented HyBrTec process recovers green hydrogen from negative-valued carbonaceous waste for a projected cost of \$2/kg while providing a 15% capex ROA. Waste feedstock includes: sewage, manure, forest & agricultural residuals, kitchen-waste, paper, textiles, municipal solid waste and plastics, all of which are an economic and environmental burden to process and dispose.

HyBrTec recovers the hydrogen in two steps. First, wastewater and organic solidwaste are reacted (burned) with bromine to produce 175 C heat, carbon-dioxide and hydrobromic acid. The acid is then electrolyzed to produce recyclable bromine reagent and hydrogen as illustrated at right.



In addition to useful process heat, HyBrTec's by-product carbon-dioxide is non-anthropogenic and with the hydrogen can be used to synthesize conventional fuels without GHG emissions.



Compared to water electrolysis, HBr electrolysis exploits fast kinetics and low energy requirements with inherent advantages due to differences in the ionic two-body hydrogenbromide bond and the covalent three-body bonds between hydrogen-oxygen-hydrogen in water. Along with lower catalyst cost, HBr electrolysis also allows higher electrochemical compression. With water electrolysis output hydrogen pressure is limited to around 400 psi due to the risk of hydrogen and oxygen mixing. In contrast, HBr electrolysis allows electrochemical compression of hydrogen to 10,000 psi. HBr electrolysis systems are similar to the PEM systems used by the chlor-alkali industry to produce chlorine, sodium hydroxide and hydrogen electrolyzing brine.

HyBrTec's advantages are undeniable: Hydrogen has an energy content (HHV) of ~39 kWh/kg, which fueling a 50% efficient fuel cell can deliver ~19 kWh/kg. Water electrolysis requires ~50 kWh/kg of hydrogen. In contrast, hydrobromic acid electrolysis requires ~18 kWh/kg of hydrogen with strong dependence on electrolyte concentration and temperature. Hydrogen from hydrobromic acid, which is then reacted in a fuel cell with oxygen affords a theoretical round-trip efficiency >100% (19/18) without including energy content of the waste feedstock. In contrast, hydrogen from water electrolysis yields a round-trip efficiency ~38% (19/50).

In addition, hydrogen bromide electrochemistry is highly reversible (2HBr  $\leftrightarrow$  H<sub>2</sub> + Br<sub>2</sub>), affording an efficient energy storage capability by converting electricity into storable chemical energy that can later be converted back into electricity. Elestor <u>https://www.elestor.nl/news/</u> is developing energy storage systems that exploit the reversible HBr electrochemistry in a flow-battery. The flow-battery will also use electrochemical compression to store and convey hydrogen at high pressures, providing additional benefits in operating cost and efficiency.



#### CHEMERGY

**The Opportunity:** To further our country's sustainability, Congress has passed the \$433 billion 2022 Inflation Reduction Act, which includes: 1) developing and promoting 'clean' hydrogen as an alternative to fossil fuels, 2) developing energy storage to improve the dispatchability and economics of renewable energy, and encourage the adoption of distributed microgrids, 3) setting goals to accelerate domestic manufacturing of clean energy systems, 4) \$8 billion to introduce Hydrogen Hubs across U.S., and 5) a Clean Hydrogen Production Tax Credit, a \$3/kg tax credit for green hydrogen. In addition to producing low-cost green hydrogen, HyBrTec offers:

1. Biowaste is ubiquitous and an economic and environmental burden. It cost \$40-200/ton to dispose, which also presents a future liability. In Florida alone, land-spreading sewage sludge concentrates toxins and heavy metals in feed crops that get into livestock and milk, promotes toxic algae blooms that kills wildlife and makes people sick, annually costing rate-payers \$20 million in tipping fees and taxpayers over \$100 million to clean-up the resulting environmental contamination. Composting biowaste emits hydrogen-sulfide and methane that is 28 times worse GHG than carbon dioxide, and burning releases carcinogens and toxins into the atmosphere. Yet, biowaste contains about 5 kWh/kg of stored solar energy, about the same as low-grade coal.

2. Reversable hydrogen-bromide energy storage can efficiently: mitigate cyber-attacks, weather-disruptions, demand-instability, and cost-fluctuations, promote solar & wind renewable energy resources and smart- micro-grids that provide distributed community resiliency benefits. https://arpa-e.energy.gov/technologies/projects/hydrogen-bromine-flow-battery

3. There are over 16,000 sewage treatment plants in the U.S., which along with confined animal feeding operations, municipal landfills, forest and agricultural industries provide sites burdened with wet organic waste that can become well-distributed national "Hubs" for green hydrogen production and energy storage.

HyBrTec advantages include: meeting DOE green hydrogen goals, eliminating waste disposal issues, co-production of green conventional fuels and electrical energy storage in distributed microgrids; benefits that are not available with other technologies. Chemergy's HyBrTec linked to energy storage will meet the DOE "Moonshot" goal of \$1/kg within three years not a decade.

Florida has over 300 sewage treatment plants that annually land-spread over 65,500 tons of sewage sludge, whose nutrient run-off promotes toxic algae growth that contaminates Florida's waters impacting essential hospitality industries. HyBrTec recovers 150+ kg of hydrogen from a ton of dry biosolids. Thus, the biowaste that is now contaminating Florida's waters, could be processed into over 10 million kilos of green hydrogen with the energy (Btu) equivalent of 10 million gallons of gasoline (gge) annually. Miami-Dade Water and Sewer Department (M-DWASD) produces over 600 tons of sewage sludge daily. In January 2020 the Florida Department of Environmental Protection (FDEP) approved a pilot demonstration of HyBrTec processing MD-WASD sewage sludge. Due to pandemic delays, the program began in March 2021 with FDEP funding \$1.15 million. Subsequent to budgeting and selecting suppliers, in December 2021 Chemergy contracted with Xytel <u>https://xytelcorp.com/</u> to engineer, procure and construct the pilot system, which will be commissioned and displayed in March 2023.

The Florida 2020 Clean Waterways Act supports infrastructure improvements to end landfilling and to prevent raw sewage discharges due to power outages. This legislation provides an opportunity for Chemergy to solve a major Florida economic and environmental problem by recovering low-cost green hydrogen from sewage sludge as a sound alternative to land-spreading and by co-providing an energy storage capability that will mediate power disruptions.

## CHEMERGY

**Reducing GHG Emissions:** The 2022 Inflation Reduction Act includes developing clean hydrogen, which has led to the DOE "Moonshot" goals. Green hydrogen is from renewable resources including: water electrolysis with renewable electricity, and from biomass without fossil-carbon, or GHG emissions. Blue or grey hydrogen is from fossil-fuels with carbon sequestration (blue) or without (grey). In addition to recovering green hydrogen from wet-biowaste, HyBrTec can recover what was blue or grey hydrogen and sulfur or sulfuric acid from hydrogen-sulfide (H<sub>2</sub>S) without GHG emissions. Any hydrogen, which was originally green, blue or gray, from H<sub>2</sub>S without fossil-carbon emissions, would be clean and green.

H<sub>2</sub>S is a highly corrosive, flammable gas, and a regulated pollutant with the toxicity of cyanide. It contaminates oil- and gas-wells, is produced in the desulphurization of refinery products, and is a byproduct of anaerobic digestion at wastewater plants, landfills, and agri-digesters. H<sub>2</sub>S contaminates bio-syngas products, and removing it at its production site lowers the cost of methane and refinery-products, promotes bio-syngas use, reduces sour-gas flaring and GHG emissions. Eliminating H<sub>2</sub>S *and* recovering its hydrogen content provides an untapped, low-cost, green hydrogen source that supports the Federal "Act" and DOE GHG abatement missions.

Chemergy has investigated a process that eliminates  $H_2S$  by recovering its hydrogen ( $H_2$ ) and sulfur (S) content using thermo- and electro-chemistry. The fundamental concept came from nature. Due to ocean warming, frozen-methane clathrates melt and the gaseous-methane rises to the surface unreacted with saltwater. In contrast,  $H_2S$  from underwater thermal vents dissolves in saltwater and the sulfur is used by bacteria in a chemosynthesis food-chain that supports tubeworms and other crustaceans.

H<sub>2</sub>S forming sulfur in saltwater while methane bubbles-up to the surface prompted Chemergy to investigate using bromine (Br<sub>2</sub>) to react with the toxic pollutant. Researchers bubbled a mixture of methane and H<sub>2</sub>S in a glass column of water and bromine. The solution was initially dark red that soon became clearer as the H<sub>2</sub>S reacted with the bromine forming clear hydrobromic acid (HBr<sub>aq</sub>) with solid sulfur deposited on the column's surface. The now sweetened methane bubbled out of solution unreacted. The process produces a weakly-bonded hydrogen-carrier hydrobromic acid and sulfur, in an exothermic reaction:

$$H_2S(g) + Br_2(aq) \rightarrow S(s) + 2HBr(aq) \qquad \qquad \Delta H^o = -30 \text{ kWh}_{th}/kg H_2$$

The aqueous HBr is then electrolyzed to recover both Br<sub>2</sub> reagent and H<sub>2</sub>:

$$2HBr(aq) \rightarrow H_2(g) + Br_2(aq) \qquad \qquad \Delta G^\circ = +18 \text{ kWh}_e/\text{kg H}_2$$

Four-times as much HBr, and subsequently four-times the amount of hydrogen, can be produced by including water as co-reactant and modifying the reactor conditions to produce sulfuric acid:

 $H_2S(g) + 4Br_2(aq) + 4H_2O(I) \rightarrow 8HBr(aq) + H_2SO_4(aq)$   $\Delta H^\circ = -24 \text{ kWh}_{th}/kg H_2$ 

Chemergy's bench-top R&D demonstrated:

- 1. Reaction between bromine and H<sub>2</sub>S in solution occurs readily.
- 2. Hydrobromic acid, sulfur (or sulfuric acid) are the products of the reaction(s).
- 3. Hydrocarbons do not react with bromine or hydrobromic acid at process conditions.
- 4. At low temperatures (30°C), reactions are fast, yield is high, and significant heat is released; this reduces the system size and allows heat to be used to reduce electrolysis energy.
- 5. Preliminary economics projected a \$1.5/kg hydrogen production-cost with a 25% ROA.

# CHEMERGY

As illustrated at right, the process begins by injecting a gas stream containing  $H_2S$  into a reactor containing a bromine-rich and dilute hydrobromic acid (HBraq) solution. The bromine and  $H_2S$  react to produce sulfur, heat and more concentrated acid. The now diluted bromine and concentrated HBraq solution and sulfur slurry is pumped to a filter-press/dryer where the sulfur is separated, washed, dried, and removed. The concentrated HBraq is electrolyzed to produce hydrogen and regenerate the original dilute HBraq and now bromine-rich solution, which is recycled back to the reactor to continue the process. The hydrogen and sulfur byproducts are further treated to recover any trace bromine and HBraq that are return to the process.





Petrochemical processing requires hydrogen to remove sulfur as  $H_2S$  from gasoline, diesel, jet fuel and oils through hydrodesulphurization. The amount of hydrogen consumed depends of the sulfur content of the crude oil. Desulphurization requires ~2 kg of hydrogen for every ~32 kg of sulfur removed, producing 34 kg of  $H_2S$  that due to its toxicity, must be further processed into sulfur and water or sulfuric acid.

In the U.S. ~125 oil-refineries refine ~18 million barrels of crude oil daily consuming ~3.2 million kg of fossil hydrogen to remove sulfur from their products. Most of the hydrogen is from Steam Methane Reforming (SMR). SMR is currently the lowest cost solution at \$1.40-2.40/kg hydrogen; however, it releases ~7 kg of GHG carbon-dioxide for every kg of hydrogen produced. HyBrTec allows recycling hydrogen, valued at over \$1 billion, lost in desulfurization and would also reduce ~8.2 billion kg of U.S. carbon-dioxide emissions annually.

Buying or producing hydrogen for desulphurizing refinery products in the U.S. is a "stay-inbusiness" investment. The investment does not yield a ROI, it simply enables the refinery to meet standards on the sulfur content of fuels and thereby remain in business. Globally, refining requires ~4 billion kg of hydrogen for desulphurization of products, which requires releasing ~28 billion kg of carbon-dioxide reforming fossil fuels into grey hydrogen. The sulfur content of crude oil is increasing and likely to continue in the foreseeable future.

Chemergy's process can also sweeten sour-gas by removing its H<sub>2</sub>S content without effecting the valuable hydrocarbons as an alternative to flaring. Flaring, illustrated at right, is the practice of burning gases contaminated with H<sub>2</sub>S that are uneconomical to collect and sell or present a safety problem. When sour-gas is co-produced at oil wells, operators will often flare the gas to convert the highly toxic H<sub>2</sub>S contaminate into less toxic compounds, including sulfur dioxide and nitrogen oxides that cause acid rain, air pollution, and soil destruction, impacting the metabolism of plants and worsening citizens' health issues.



Global flaring releases ~400 billion kg of fossil-carbon annually. The World Bank reports 13.5 to 15.3 billion kg of sour-gases are flared annually, valued at ~\$30.6 billion, clearly illustrated here: https://viirs.skytruth.org/apps/heatmap/flaringmap.html#lat=29.43243&lon=15.26825&zoom=3& offset=15

### THEMERGY

If flaring isn't possible sour-wells are capped. Removing H<sub>2</sub>S at the well-head allows reopening these wells and the monies associated with the value of the now sweetened gas in addition to the value of hydrogen and sulfur or sulfuric acid. Recovered hydrogen does not require additional costs for storage but can simply be added to the now-sweetened gases, contributing its Btu content and significantly reducing NOx emissions when burned. H<sub>2</sub>S is also a byproduct of sewage treatment and dilute (non-lethal) but significant quantities are produced in landfills and anaerobic digesters. Eliminating H<sub>2</sub>S and producing hydrogen from these sources will encourage exploiting untapped sour- and bio-gas resources.

Chemergy's process eliminates the poisonous  $H_2S$  contaminate in sour-gas without affecting the valuable hydrocarbons and allows the recycling of hydrogen lost in hydro-desulfurization. HyBrTec processing  $H_2S$  is simpler than processing wet-biowaste that is at elevated (175°C) temperatures and pressures; however, both feedstocks exploit efficient hydrogen-bromide electrochemistry that can co-provide an efficient energy storage capability and requires considerably less energy than water electrolysis. Chemergy anticipates meeting the DOE "Moonshot" goal of \$1/kg hydrogen by processing refinery and sour-gas hydrogen sulfide, and eliminate the emission of billions of kg of GHG.

**Technology's History:** In 2000 the DOE funded two Cooperative Research and Development Agreements to demonstrate: 1) With NREL, the on-sun production of HBr, from water and bromine with solar energy, and 2) With National Power from the UK, HBr based energy storage. In 2010 our R&D demonstrated the recovery of hydrogen, sulfur or sulfuric acid from H<sub>2</sub>S without affecting valuable hydrocarbons. In 2011 the DOE and Florida Hydrogen Initiative funded benchtop R&D that recovered hydrogen from cellulose. In 2015 the California Energy Commission funded an R&D program that: 1) demonstrated the recovery of 100 kg of hydrogen from a dry-ton of sewage sludge, 2) designed a pilot system, 3) projected revenue, cost and income of commercial systems, and 4) completed technical evaluations including mass & energy balances by Lawrence Livermore National Laboratory. In 2020 the Florida Department of Environmental Protection approved a \$1.15 million, two-year pilot program to process sewage sludge for Miami-Dade Water and Sewer Department.

**Technology's Future:** After addressing community and industrial waste treatment, energy storage and green hydrogen needs, by 2030 Chemergy plans to commercialize a 'bullet-proof' ~\$15K home appliance for processing household toilet, kitchen, yard and mail waste into green hydrogen, heat, potable water and on-demand electricity. The appliance would have active monitors to predict potential failures, built-in passive neutralization of any leaks, and be capable of processing ~15 kg of biosolids and ~15 kg (~4 gal) of wastewater into ~3 kg of hydrogen daily.

