

Hydrogen from Steam/CO₂ Reforming of Waste

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The Hydrogen Economy Has Arrived: Globally today the commitment for the coming hydrogen economy is here. And for us in California, we continue to stay on the leading edge. We are demonstrating hydrogen engine vehicles, fuel cell hybrids, hydrogen plug-in hybrids, together with hydrogen turbo-gen sets as peakers, wind turbines electrolytically producing hydrogen, etc.

Just consider the investment and interest in hydrogen-powered vehicles, whether electrically by on-board hydrogen storage powering fuel cells or powered by new hydrogen-burning internal combustion engines. An excellent listing of commercial, pre-commercial, and concept vehicles can be found on the website: www.hydrogencarsnow.com, (1), wherein 42 hydrogen vehicles are listed representing 12 major automobile companies, 6 countries, and covering the range of commercially attractive and practical technologies for cars and trucks in Table 1 below.

TABLE 1: INTRODUCTION OF HYDROGEN CARS AND TRUCKS

Company	Elect.Motor	Battery	Plug-In	H2 Tank	Max Speed	Year
GM-Chevy Equinox	120 kW	LiO 60 mi	yes	300 mi	100 mph	2012
GM- Volt			yes	none		2009
GM HydroGen-3	60 kW	NiMH 35 kWh	No	250 mi		
Ford - Edge		25 mi	yes	175 mi		2015
Ford – Focus-FuelCell	65 kW	NiMH	No	200 mi	80 mph	2007
Chrysler- EcoVoyager	200 kW	LiO 16 kWh		300 mi	115 mph	
Honda-FCS Clarity	100 kW	LiO	yes	270 mi	100 mph	2009
Toyota- FCHV-5	80 kW	NiMH 21 kWh	No	180 mi	96 mph	2007
Audi A2H2	66 kW	NiMH 38 kWh	No	137 mi	109 mph	
BMW-Hydrogen-7 *	191kW ICE	no	No	125 mi	143 mph	2009
VW Touran HyMotion	80 kW	NiMH	No	100 mi	87 mph	2006
Mazda-5 RX8			No	124 mi		2008
Mercedes-F-Cell Car	72 kW			250 mi		
Hundai Hylord FCEV	80 kW	LiO	No	90 mi	93 mph	2004
Hundai Iblue				360 mi	100 mph	2008
Kia Sportage	80 kW	LiO	No	205 mi	93 mph	
Nissan X-Trail FCV	90 kW	LiO	No	311 mi	90 mph	2005

* Is dual-fuel selectable

See concept cars: www.hydrogencarsnow.com

Take some examples. The FORD EDGE with HYSERIES DRIVE brings the latest fuel cell technology to life in a battery powered plug-in hybrid with a 15 kW fuel cell that operates as an on-board charger. The vehicle operates in "battery only" mode for the first 25 miles. H₂ storage earlier with 7,000 psi then with 10,000 tank. The fuel cell's sole function is to recharge the vehicle's lithium

ion battery pack as needed, allowing this break-through technology to work like a portable generator, instead of an engine, as has been the case in previous fuel cell powered vehicles. The combination provides a 200 mi range. Plug-in recharge is 3 hrs with 220 vac and 10 hrs with 120 vac. The EDGE is to be fully commercial 2015-2017.

The most recent introduction is the Honda FCS Clarity: Leasing in Los Angeles in summer '08 at \$600/mo, Using H₂ filling stations in LA increasing up from 5 now, it uses the new "V-Flow" fuel-cell stack driving a 134 hp electric motor on front-wheel drive. There is a Lithium oxide (LiO) battery pack for regenerative braking. It achieves 100 mph with 270 mi range with an onboard H₂ tank that is 68 mpg gasoline equiv. Since a zero-emissions car is only as green as the source of that energy, we feel green hydrogen (like what we produce) is better than hydrogen produced from fossil fuels. If green hydrogen is not available locally, then Honda, in a thought process somewhat similar to our own, makes available a solar electrolysis home unit to make the green hydrogen.



Figure 1: Honda Hydrogen Fuel Cell FCX Clarity

Besides the hydrogen fuel cell-based vehicles, there are also those that burn hydrogen in a specially optimized internal combustion engine, such as the BMW 7-Series luxury vehicle. These BMW Hydrogen7's are being tested in Europe, Australia and the US as part of a world marketing thrust. Up to 25 Hydrogen 7's will be sent to the U.S. They are clearly positioned to prove liquid hydrogen as a practical source of energy for production cars. BMW's V12 engine produces 191 kW of power and 390 N-m of torque and accelerates from 0–100 km/h in 9.5 seconds. Top speed is limited electronically to 230 km/h. A specially designed crash-proof tank houses the 8 kg of liquid hydrogen that powers the car. Designed as a seamless dual-fuel vehicle, it has a range of 200 km on hydrogen and 500 km on gasoline. A one-touch steering wheel-mounted button allows the driver to switch between gasoline and hydrogen fuel, even when on the move.

Besides cars, there are also buses and trucks appearing around the world. Fuel Cell zero-emission buses currently operate in daily revenue service at three California transit agencies. Since 1999, these members of the California Fuel Cell Partnership have placed nine fuel cell buses into operation and they have traveled more than 165,000 miles on California's roads and highways. In the Palm Springs area, SunLine Transit Authority operates one fuel cell bus, and Oakland's AC Transit operates three buses. All are Van Hool buses that use UTC Power fuel cells. ISE Corporation was the bus integrator. In the Silicon Valley, Santa Clara Valley Transportation Authority operates three buses powered by Ballard Systems fuel cells. Other fuel cell bus demonstrations in California include the U.S. Department of Transportation, U.S. Department of Energy, California Energy Commission, California Air Resources Board, Toyota, and Chevron.



Hydrogen Fuel Cell Delivery Services Vehicles

Ford makes a large hydrogen combustion engine, the F-450, which was introduced in Shuttle bus service in Florida and can be used on the standard medium-size truck chassis. HydrogenEngines Inc, makes F150 and 250 engines that are optimized for hydrogen fuel to be used in smaller light trucks and buses. Delivery services are moving to hydrogen, such as United Parcel Service with their new Sprinter, serving Los Angeles.

Figure 2: The UPS Sprinter and Mercedes Benz A-Class

The Hydrogen Fuel Supply Infrastructure:

California's "Hydrogen Highway" system that was announced 5 years ago is an important step for the evolving hydrogen economy. Earlier this year the state legislature approved \$6.5 million (a small amount) for the California hydrogen highway effort. This includes funding for three new stations that will be cost-shared with industry. Figure 3 is a map of California showing H2 stations running and planned.

Figure 3: Hydrogen Highway Map

Federal and State incentives for producing hydrogen from renewable sources and for building the infrastructure for dispensing this hydrogen for vehicle fuels are critical. Also we anticipate soon we will have a tax on carbon emissions to provide the economic drive for everyone to reduce or eliminate our carbon footprint. There are now 17 states with some sort of cap in place on auto or power plant carbon



emissions. We recommend obtaining hydrogen from renewable and sustainable sources. At Intellergy, for over two decades we have demonstrated the production of green hydrogen from a large variety organic sources. This is done without any combustion of feedstock or external fuels, with their undesirable greenhouse gas emissions.

Green Hydrogen:

Two of our recent activities have involved steam reforming feedstocks with quite different characteristics. One, medical waste, involved plastics, paper, and other substances. A second was a homogeneous agricultural feedstock. In both cases, we were able to achieve a high degree of conversion to hydrogen. It is also important to note that the technique we use sequesters a high proportion of the carbon that goes through the system into an inert and sterile residue, suitable as fill for construction materials. This is a large plus on the climate change side.

At the last hydrogen conferences, we showed how significant biomass can be in making green H₂ and in reducing greenhouse gases (2). For the U.S., the use of biomass for the production of hydrogen can eliminate U.S. oil imports. There is enough household waste at 5.5 lbs/person-day to fuel hydrogen fuel cell cars for every person in the U.S. And in most other developed countries their household waste can provide most of the energy needs at about 8 kWh per day. For developing countries their production of waste is less but so is their per capital energy consumption. This match almost seems to be a “universal law.”

Carbon-negative footprint: What if there could be a new technology that can remove CO₂ actively from the atmosphere without a large and complex process that could both sequester the carbon without putting CO₂ underground and at the same time supply green hydrogen for our economy, particularly vehicles. This could help solve some of our problems and can achieve a large “field-to-wheels” carbon efficiency. Our technology can do exactly this.

Here is a brief overview of the carbon footprint of our technology: fill for construction materials, water for irrigation, fertilizer as residue, H₂-powered harvesting & transportation without carbon emissions through use of green hydrogen.

For every H₂ fuel cell car we fuel, 0.1 tonne of CO₂ is removed from the atmosphere per year. There are 200 million cars in the U.S. that could consume 25.6 million tons of H₂ if all FC cars. There are 150 million trucks in the U.S. that could consume 256 million tons of H₂ if all FC trucks. If all the U.S. cars and trucks were H₂ fueled, about 220 millions tons of CO₂ would be removed from the atmosphere if the H₂ plants were fed all agri-biomass. The same result is achieved if we use forest bio-mass as well. Neither involves combustion and all avoid air pollution.

Fuel Cells Using Our Syngas: The fuel cell option has positives and negatives as follows: It is true that syngas is typically 55% H₂ and 33% CO (in high quality steam/CO₂ reforming) and will drive either Molten Carbonate and Solid Oxide fuel cells and anode electrode catalysts are not poisoned by CO. Syngas-powered fuel cells have the big disadvantage that oxygen is consumed from our atmosphere (a depleting resource) in the cathodic electrochemical conversion, and from the anodic conversion CO₂ is released that is very difficult and expensive to sequester. Plus, the CO₂ from the anode is commonly commingled with the nitrogen from the cathode, so the CO₂ is unacceptably diluted. Under DOE’s SECA program several companies have succeeded in

redesigning their fuel cells to keep the nitrogen from contaminating the CO₂. This adds considerably to the fuel cell cost but deals with the problem. So the SECA program fuel cells now produce relatively pure CO₂. But the concept of CO₂ injection under pressure underground is risky from both the human safety and environmental impact standpoint, is expensive, and may become very unpopular with the public. In conclusion, sadly, the negatives are beginning to loom unacceptably large and may cause rejection of this once popular approach backed by the fossil energy-focused coal and petroleum folks. We feel there is a better way.

The Steam/CO₂ Reforming Option: No fuel cell conversion or combustion steps are involved. Intellergy has developed and has been awarded domestic and foreign patents over 25-years on a new process technique that produces hydrogen and a carbon-sequestering by-product. Our steam/CO₂ reforming is conducted in a rotary kiln heated only by inert hot gas generated from process waste heat and involves no combustion. The raw, high quality syngas is produced in this first step and the syngas is further refined in a second stage steam reformer. From there the gas is processed in two steps to produce steam, heat, carbon sequestering residue and green hydrogen. The process diagram below simply illustrates this novel approach.

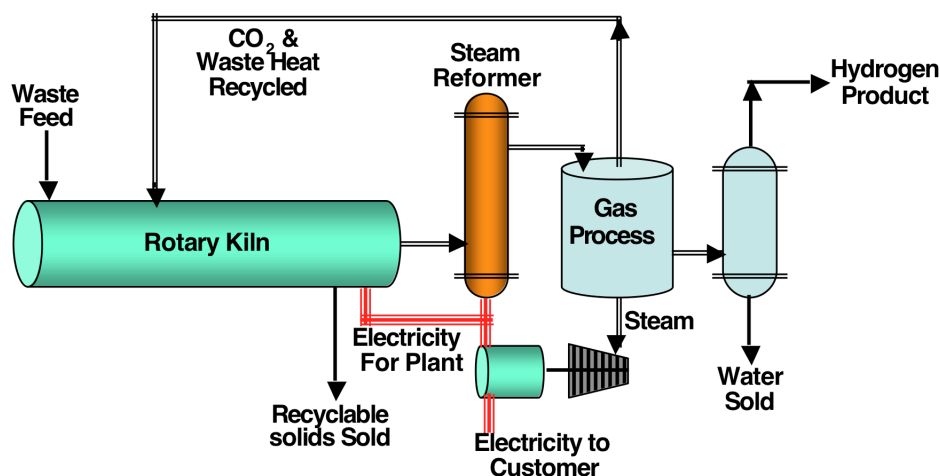


Figure 5: Simplified Process Flow Diagram

Medwaste Processing: The purpose of this continuous flow pilot plant was to completely characterize and monitor the quality of the syngas produced from the steam/CO₂ reforming operation with medical waste from the Bay Area. This waste was continuously fed to a rotary kiln to produce syngas which was passed through the appropriate filters to achieve purity of such high quality to be fed to a high-temperature fuel cell or equivalent process step. This testing was accomplished using stack gas sampling similar to standard EPA methods and the results of these tests and syngas compositions have been summarized and are presented in a test report.

An indirectly-heated screw-conveying kiln was fitted with a steam/CO₂ reformer reactor and quench scrubber/condenser. Shredded medical waste that was microwave-sterilized was fed to the electrically heated screw at 2.58 lb/hr. It was heated to a temperature high enough to thoroughly convert the waste and effect a mass reduction of 84.5%. The process was run and the gas sample collected in order to generate enough off-gas for sample collection. Offgas was sampled for:

- ∞ Polychlorinated Dioxins and Furans
- ∞ Semi-Volatile Organic Compounds (SVOCs)
- ∞ Volatile Organic Compounds (VOCs)
- ∞ Sulfur compounds
- ∞ CHONs (CO, CO₂, H₂, O₂, N₂, C₂-C₇ hydrocarbons) and lower & higher heating value
- ∞ Hydrochloric Acid (HCl) and Chlorine (Cl₂)

The key conclusions were:

[1] The Syngas produced was very clean with H₂ over 60%, CO = just under 20%, CH₄ = just under 8%, CO₂ = at 10%, and ethane = 0.5%. This is quite appropriate for high temperature fuel cells or equivalent.

[2] The lock-hopper feeder concept worked well and is scalable for full-size-range commercial plants.

[3] The feed conveyor within the first stage steam/CO₂ reforming kiln did not ever plug or become restricted by the plastic portion of the medwaste for the entire length of the test.

[4] The exit lock-hopper also worked well with only minor amounts of solids retained.

[5] The gas cleanup system worked well, removing both the acid gases such as HCl and H₂S as well as entrained particulate, which floated to the top and could be skimmed off.

[6] The nature of the solids from syngas cleaning were such that they could be recycled back into the kiln for further steam/CO₂ reforming. This kiln and reformer operation and process configuration option is available to eliminate these solids.

[7] The heavy metal contaminants in the solids strongly suggest that they come from dissolution of stainless piping during the testing and may be lower with full-sized units with a higher grade alloy tube.

[8] The final value for Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans in the product syngas is 0.0041 pptv or 0.054 ng/m³ TEQ. This shows that the syngas is very clean and low in risk to the public should it be released during an accident.

Agri-biomass Processing: The biomass was strictly cellulosic and contained no edible food materials. This was selected to demonstrate that our process can handle cellulosic feedstocks. The cellulosic feedstock was carefully analyzed by ultimate and proximate analysis for fixed carbon at 22.59wt%, volatile carbon at 72.03 wt%, and ash at 5.38wt% on a dry basis with sample moisture at 3.87%. Elements are given by the empirical formula: C₁H_{1.344} O_{0.506} N_{0.031} S_{0.002}. The molecular weight was determined to be 21.938. There was a 66 ppm level of chlorine detected, undoubtedly from mineral sources available to growing the crop.

The Syngas produced was very clean with H₂ over 59%, CO = around 30%, CH₄ = around 5%, CO₂ = 3%, and ethanes = 0.5%. This is quite appropriate for high temperature fuel cells or equivalent. Rotary kiln operation was exceedingly good owing to the relatively uniform nature of the size-reduced material. The material was processed efficiently, with the solid residue consisting almost entirely of the residue and fixed carbon at 29.65wt%. The above results were excellent, showing that very high production of hydrogen is possible and that it can be purified into a high quality fuel grade, green hydrogen fuel.

Using the Intellergy patented steam/CO₂ reforming process, a huge range of biomass can be processed successfully to produce a high quality, green hydrogen fuel for vehicles or for commodity hydrogen sales, or alternatively producing somewhat less hydrogen but at the same time sequestering carbon in useful products; thus, avoiding the problems of injecting CO₂ underground.

Impact of biomass to green H₂ on future H₂-economy: Table 2 shows the huge energy sources that are possible with available biomass and waste streams. This would have a very major impact on our import energy crisis in the U.S.

Table 2: Energy Impacts of Available U.S. Feedstreams

Sector	Total dtpd	Energy, GWe	Oil Equiv. Mtoe/yr
Medical	29,000	29	56
Beef	180,500	18	35
Poultry	120,655	12	23
Diary	13,900	14	27
Pork/Lamb	11,900	12	23
MSW	962,500	100	194
Sewage Sludge	157,500	16	31
Total Feed	1,481,355	201	389

To estimate the impact on the future H₂ economy, consider the amount of organic material available. Even with a moderate penetration into the marketplace, there would be a great deal of green hydrogen produced. In 1999 globally there was 400 billion m³ or 35.2 billion kg per year of fossil based hydrogen produced (4). Clearly, our approach can provide a lot of hydrogen for the worldwide hydrogen economy without a harmful carbon footprint eliminating at least 1.3 billion tons of CO₂ per year, or over ¼ of all U.S. CO₂ emissions.

Advantage of multiple income streams: Biomass incineration plants do not pay out well because they cannot compete with fossil plants to produce electricity on a competitive basis. Some of the larger mass burn plants have also co-generated steam or heat. The value of this heat is far less than the value of the electricity. The electricity income is simply not sufficient with approximately 30% fuel-to-electricity efficiency, the cost of operating such plants is too high. This problem can be corrected by producing a multiplicity of income-generating products such as H₂, carbon-based products, steam, heat, etc. The process can provide the hot gas to drive the Brayton turbine co-gen system and its waste heat can be used to make steam and low grade heat.

Also important is the fact that the syngas that is produced by the reforming process is multiply used to produce a pure hydrogen stream to be sold as a commodity fuel and carbon-sequestering products.

References:

1. See listing of hydrogen cars: www.hydrogencarsnow.com
2. F. H. Schwartz and T. R. Galloway, "Producing Hydrogen from Waste," 2006 Hydrogen Production & Storage Forum, Vancouver, B.C., Canada, Sept. 11-13, 2006.
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4. Rifkin, Jeremy, "The Hydrogen Economy," Penguin-Putnum, N.Y., 2002.