

Ending Our Hydrogen and Ammonia Addiction to Fossil Fuels

 \blacksquare he world uses at least 50 billion kg of H_2 per year, with nearly 20% of that (9 billion kg) used in the United States. More than half of that H₂ is produced from natural gas, with most of the rest made using other fossil fuels. If we are to change the upward slope of CO₂ emissions, the source of this H₂ needs to change. While using natural gas minimizes the carbon footprint relative to other fossil fuels, the cost of large scale solar power is falling to \$0.03 kWh or less, and thus, a greater effort is needed to lower the costs of producing H₂ from water. Success in producing inexpensive H₂ from water could aid in decreasing our carbon footprint for ammonia production and enable greater use of H₂ in transportation.

AMMONIA PRODUCTION IS THE GREATEST CONSUMER OF H₂ GAS

Approximately 53% of commercially produced H₂ gas is used to make ammonia, primarily for use in fertilizers, at an energy cost of ~30 GJ/tonne, or 26 GW in terms of power (electricity from 26 large power plants running continuously). A large number like this can be difficult to relate to your daily life. However, if this amount of power is converted into the energy in the food you consume every day (2000 calories per day or 100 W/person), it is equivalent to enough "food energy" to sustain 260 million people, or ~80% of the population of the United States. Over the years, no process has been able to even come close to displacing the main method for ammonia production using the Haber-Bosch process, even though it is very energy intensive. However, due to the availability of cheap solar electricity, many researchers are now examining ways to use solar energy to directly produce ammonia by electrochemical processes. Unfortunately, to date there have not been any real successes. The main approach at present for producing ammonia using solar energy is water splitting to produce H₂, with the H₂ then used in the Haber-Bosch process. Such an approach is already being investigated at the scale of a 2.5 MW solar plant being built by Yara, the world's largest producer of ammonia, in Australia. At best, however, the plant will reduce CO₂ emissions by only half (http://science.sciencemag.org/ content/361/6398/120.long).

■ H₂ CURRENTLY USED BY REFINERIES COULD GO A LONG WAY TOWARD POWERING FUEL CELL VEHICLES

It is commonly reported that refineries use ~20% of the hydrogen produced in the United States, but this likely does not consider hydrogen produced on site by the refineries for their own use (i.e., they consume additional H₂ that is not commercially available). Refineries in the United States are reported to consume \sim 3.8 billion kg of H₂ annually to produce gasoline and other products, which would double the amount of H₂ used in the United States for this purpose. H₂ fuel cell vehicles being sold in the United States get ~60 miles/kg of hydrogen, which is an energy efficiency that is >3 times that of gasoline-powered light duty vehicles (1 kg of H_2 is equal to \sim 1 gal of gasoline). Thus, the amount of H₂ already being used at

refineries could replace ~7% of cars on the road that use gasoline with fuel cell vehicles.

Solar and wind power could provide a significant source of H₂ needed for transportation coupled to water splitting, but waste biomass could play an important role as well. The U.S. Department of Energy estimates that ~1.3 billion tonnes of dry biomass could be made available for transportation fuels without impacting food production. Stoichiometric conversion of 1 billion tonnes of cellulose in biomass into H₂ could provide about almost the same annual energy as that consumed by light duty vehicles, suggesting it might be able to sustain these vehicles. Fuel cell vehicles will have energy efficiencies even greater than those of current gasoline vehicles; however, cellulose cannot be converted to hydrogen at either stoichiometric percentages or at complete energy efficiencies. Even with these uncertainties, production of H₂ from biomass and solar could have a great impact on a hydrogen "transportation" economy.

Development of a hydrogen transportation infrastructure would take decades and require investments by both businesses and governments. Businesses usually cannot justify such investments without certainty of a payback within 3-5 years (which is unlikely to occur), and government support has been too unstable to see how support could be guaranteed to last past a single federal administration (even assuming two presidential terms of 8 years). Thus, a long-term collaboration to make this happen could occur only through a truly revolutionary change in public support.

■ H₂ FROM WASTEWATER TREATMENT PLANTS

A small but significant effort to address H₂ production could be made at the local level using our used water treatment plants for H₂ production coupled to treatment or ammonia recovery following treatment. Against the backdrop of all these enormous numbers for H2 production, the small recovery of ammonia from wastewater would seem to be unimportant due to the relatively tiny concentrations of ammonia in used waters. However, this ammonia source has to be viewed within the context of energy costs for used water treatment. Before the water leaving our homes and other sources can be reused, it must be treated to remove organic matter, ammonia, and other contaminants. Recovering energy from the organic matter in wastewater during treatment seems logical given that the organic matter content is 2-5 kWh/m³, and many technologies are being investigated to do that based on electricity, hydrogen, or methane production. Conventional treatment uses ~0.6 kWh/m³ of water, with some treatment plants engineered to minimize power consumption already achieving energy self-sufficiency. Ammonia is usually removed during treatment at these plants by its destruction and biological conversion to nitrogen gas, which consumes energy.

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However, there is an energy value of that ammonia. On the basis of the energy needed to make ammonia using the Haber–Bosch process, 30 mg/L ammonia is equivalent to 0.25 kWh/m³, which is nearly half the energy used for conventional treatment. Recovery and local reuse of that ammonia could have an impact on energy use considering all aspects of ammonia production and transport around the world.

■ THE BOTTOM LINE

Reducing our CO_2 footprint cannot move forward without a large, dedicated effort to produce ammonia from carbonneutral sources. A large, international effort is needed to cut the tie between H_2 production and fossil fuels.

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Notes

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