Comments on *Potential Roles of Ammonia in a Hydrogen Economy – A Study of Issues Related to the Use of Ammonia for On-Board Vehicular Hydrogen Storage*

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According to the USDOE white paper, *Potential Roles of Ammonia in a Hydrogen Economy – A Study of Issues Related to the Use of Ammonia for On-Board Vehicular Hydrogen Storage,* by G. Thomas and G. Parks, "DOE does not plan to fund R&D to improve ammonia fuel processing technologies for on-board use on light weight vehicles at the present time." The reason is that ammonia-cracking units capable of supplying the ultra-pure hydrogen needed by PEM fuel cells are too bulky, too heavy and run at too high temperature to be contemplated for on-board automotive use. Thomas and Parks advise, in other words, that because one cannot foresee when it will be feasible to mate ammonia-as-fuel with PEM fuel cell cars, DOE should put off studies of ammonia "processing" for on board vehicular hydrogen storage.

Nonetheless, it is practical to store energy at much higher density in an ammonia- as against a hydrogen-storage system. Ammonia, like hydrogen, is carbon-free, and ammonia production is a well-established, economical technology (with Haber-Bosch synthesis about 60% energy efficient). Given these advantages, it would be a mistake of great moment to disregard any serious possibility of an ammonia-energized transportation system. It is therefore important to look beyond Thomas and Parks' conclusion that the ammonia/PEM fuel cell combination is unpromising, to other opportunities to take advantage of ammonia as fuel. We suggest, accordingly, that ammonia-as-fuel studies be supported by DOE. They should be directed toward automotive engines energized by *less-,* or *unprocessed* ammonia, particularly internal combustion engines (ICEs), toward ammonia-tolerant or direct ammonia fuel cells, and, importantly, toward safe on-board ammonia storage. Based on current knowledge, such R&D has a good chance of success in the near term, and a potentially huge payoff.

Closest to realization, for ammonia-fueled transportation, are efficient, clean, internal combustion engines. In spark-ignition mode, ammonia has high octane (110-130). It has also shown promise in assisted diesel (Army research) and in homogeneous charge compression ignition (HCCI) combustion (van Blarigan, Sandia). Clean exhaust, i.e. elimination of NO_x emissions in the case of ammonia combustion, can be readily achieved using a two-way catalyst that combines uncombusted NH_3 and NO_x to form benign N_2 and H_2O. Such catalysts exist today, developed to clean NO_x from diesel exhaust (selective catalytic reduction or SCR). Indeed, a catalyst might not even be necessary, since during NH_3 combustion NH_3 and NO_x are in contact at elevated temperatures where catalysts are not needed for the reaction to go forward (Selective Non-Catalytic Reduction (SNCR)).

Alternatively, one can use modest amounts of ammonia as a source for on-board H_2 to improve the efficiency of spark ignition engines. Partial cracking of NH_3 over Ni catalysts can be accomplished at modest temperatures (>300 C). Adding small amounts of H_2 to a lean gasoline-air mixture extends the flammability limit of the mixture. This allows higher compression ratios (higher efficiency), colder combustion temperatures (lower NO_x production), and lower throttle losses (higher efficiency; Hydrogen-Enhanced Combustion Engine). Partial cracking of ammonia could also be used to improve the combustion of ammonia if it were the sole fuel.

We also want to mention that H_2 with residual ammonia content is compatible with a number of higher temperature fuel cell designs like alkaline or solid oxide fuel cells. In fact, the cracking of the ammonia can happen at the electrode in form of a direct ammonia FC.

The second important, indeed unavoidable, area of research is on how to make the use of NH_3 acceptably safe without giving up too much of its advantage as a high energy density material. This is a serious issue, but one that already can be dealt with in various ways. At the extreme of maximum safety, the ammonia can be encapsulated in a highly ammoniated salt. A more conventional approach is a specially engineered pressure tank, possibly made safer by embedding a porous monolith inside it.

[The worry that ubiquitous anhydrous NH_3 will make it easier to synthesize methamphetamine is a bit of a red herring. It is already cheap and easy to evolve ammonia using widely available chemicals.]

On the economics of ammonia as an energy carrier, it is worth noting that NH_3 can be produced from "stranded" natural gas abroad that costs about 1/10th of the going rates in the US. This ammonia could then be shipped stateside and used here, whether as an automotive fuel or as an industrial source of H_2 or energy, e.g. in a power plant. Most NH_3 consumed in the US is already provided by this route. All that is needed is to scale up.

Shipping ammonia from the natural gas source, rather than the gas itself, has important advantages. The highly concentrated CO_2 byproduct of Haber-Bosch ammonia synthesis can be sequestered in the local natural gas and petroleum deposits. This form of CO_2 sequestration is not only cheap, but might more than pay for itself by enhancing the recovery of the hydrocarbon fuels. Thus, ammonia use offers energy, transportation fuel, and H_2 production without exacerbating global climate change, and looks to be one of the best options available today. Compression or refrigeration costs for NH_3 shipping are far lower than for natural gas (CNG or LNG), and unlike the latter, NH_3 is not explosive. In fact, the DOE white paper notes that “Ammonia distribution costs should be similar to LPG costs” and that “Ammonia is being considered as one of the best potential options for a one-way [hydrogen] carrier”. Use of NH_3 as a large scale energy carrier may facilitate the acceptance of NH_3 as a fuel in everyday transportation. An intermediate step might be NH_3 fueled ships or locomotives.

PEM fuel cells may eventually prove to be the optimal technology for a hydrogen economy. But bridging to a sustainable transportation fuel is a pressing matter. It is therefore important to consider alternatives in terms of cost, robustness and efficiency. All these make ICEs look competitive or better, and likely to bear fruit sooner. Fuel-cell catalysts, made of precious metals, are expensive. As Thomas and Parks note, PEM cell membranes are delicate. Despite being advertised as a 2nd law energy production system, fuel cells are dissipative. They produce electricity with efficiencies well below 100% - more like 50% at best, in fact no better than some advanced internal combustion engines.

Thomas and Parks argue that ammonia-cracking to produce hydrogen for a PEM fuel cell is not a promising approach for the near term. Impediments to ammonia-fueled internal combustion are much more modest, however, and the US would accordingly be well-served by research directed toward a transition technology based on sustainable, cheaper, more environmentally friendly (biological & biomimetic) ammonia production, safe ammonia-storage, and clean, highly-efficient, ammonia-burning internal combustion engines.

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