Solid State Ammonia Synthesis (SSAS) for Sustainable Fuel and Energy Storage Applications

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The Need for a Sustainable Fuel

There are more and less immediate reasons for developing a sustainable fuel. The immediate need for a sustainable fuel is to provide energy storage to deal with the intermittent nature of many sustainable energy technologies, particularly wind and solar power. The less immediate (but by no means far off) need for a sustainable fuel is based in humanity's need to stop emitting CO_2 from fossil fuels.

As wind and solar powered electricity generation grows, it becomes a challenge for electrical grid operators to maintain grid stability. Experience is allowing the grid operators to deal with more intermittent generation than was previously considered possible, but eventually energy storage must be used to buffer out peaks and valleys in wind and solar electricity generation and make it more "dispatchable".

In the larger picture, our best climate science tells us that we must bring our fossil fuel CO_2 emissions to zero by 2040 to avoid devastating global climate change. [2] If we do that, we will experience 2 ºC average global temperature increases, which will cause significant but bearable problems. If we instead continue our trend of increasing CO_2 emissions, we will experience 5.5 ºC average global temperature increases by 2100 (see Illustration 1). That will devastate our agricultural system by altering our seasons, precipitation, and pest populations. The increased CO_2 levels will also devastate our fisheries by lowering ocean pH, causing mass extinctions. Although it sounds alarmist, climate science indicates that modern civilization as we know it will end in the next 90 years if we don't eliminate our fossil fuel CO_2 emissions very rapidly. Although these results are belittled by some political pundits, it is important to bear in mind that climate science is not liberal or conservative; it is physics and chemistry. The biology of disease is not swayed by ones political views, and neither is the physics and chemistry of fossil fuel induced global climate change.

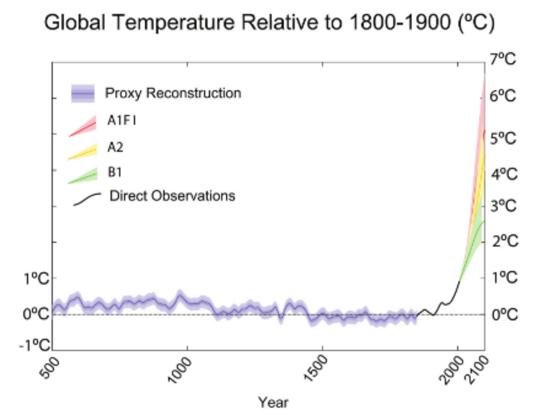

Illustration 1: Projections of global warming for different CO_2 emission scenarios. A1F1 is the "business as usual" emission scenario, while B1 requires a rapid, drastic reduction in CO_2 emissions.

Elimination of fossil fuel CO_2 emissions requires that we have a sustainable energy system to replace fossil fuels. The sustainable energy system must have three general components: *conversion*, *storage*, and *utilization*. *Conversion* allows us to convert a sustainable energy resource such as wind or solar energy into a more usable type of energy. *Storage* allows us to hold that energy until it is needed. *Utilization* allows us to use the energy for necessary tasks. Our present energy system is mostly a fossil fuel utilization system; conversion and storage were performed by biological and geological processes over millions of years. By contrast, our sustainable energy technologies are primarily conversion (wind turbines, solar panels) and utilization (fuel cells, more efficient devices) systems. Although we have some storage technologies, they are the weak component of our emerging sustainable energy system. To make the “Zero CO_2 emissions by 2040” deadline, we need energy storage systems that can link our growing wind and solar energy conversion technologies to our existing and developing energy utilization technologies.

Energy storage requirements vary according to the task being powered. Electricity generation can use fixed site energy storage. Space heating and process heating generally require electricity or a fuel that can be transported through pipes. Transportation typically has the most difficult requirements because the storage medium must have a low mass, high volumetric energy density, and large overall capacity. Although these different tasks have different specific requirements, a sustainably produced high energy density liquid fuel could work well for all of them. Ammonia, NH_3, is such a fuel.

The Fuel Characteristics of Ammonia

Ammonia, NH_3, is a compelling sustainable liquid fuel. At normal temperatures, it liquefies at approximately 150 psi and is stored in mild steel tanks or transported in mild steel pipelines. [5] The Midwestern US has over 3000 miles of NH_3 pipeline (see Illustration 2) and thousands of NH_3 dispensing stations for fertilizer, so the technologies to store and transport it are already developed. Humans can smell NH_3 well below its hazard limits, so there is no need to add an odorant to it like we do with natural gas. Unlike gasoline, it is not a carcinogen. If a leak occurs, the liquid NH_3 evaporates into a lighter-than-air gas. This allows it to dissipate rapidly, making it safer to transport than natural gas. [3]

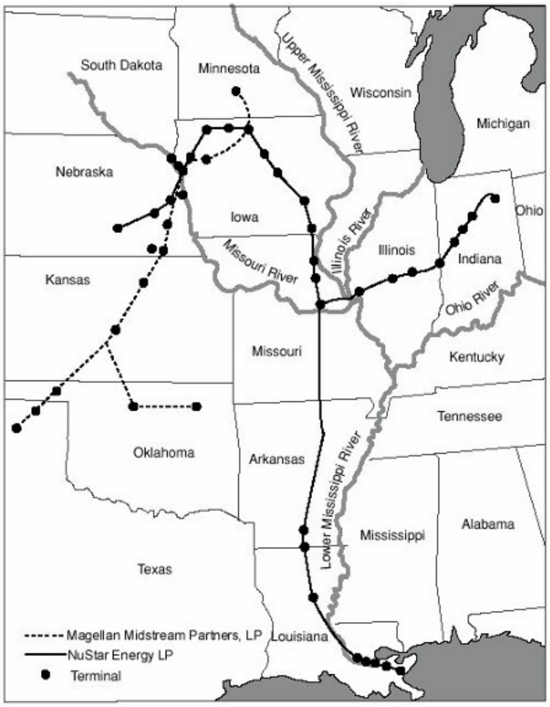

Illustration 2: Existing ammonia pipelines in the US. The pipeline is 8-10" diameter mild steel.

Liquid NH_3 has about half the volumetric energy density of gasoline. It is 17.6% hydrogen by weight, as compared to 12.5% for methanol. Its energy storage is 3 kWh/kg, or 2.7 kWh/L, which meet the 2015 “Freedom Car” goals. [4] Its volumetric energy density is high enough that we could use it to fuel internal combustion vehicles and have acceptable driving range. Although a synthesized hydrocarbon fuel could give a higher volumetric energy density than NH_3, its synthesis is would be more difficult. For sustainable chemical cycles, both fuels need to use water as a hydrogen source. NH_3 synthesis uses atmospheric N_2 (78% by volume) as a nitrogen source. Sustainable hydrocarbon fuels will have to use atmospheric CO_2 (currently 0.04% by volume) as a carbon source. [6] Large quantities of nitrogen are easily harvested from the atmosphere using existing commercial air separation units. Harvesting similar quantities of carbon from that atmosphere is more difficult due to its much lower atmospheric concentration.

Ammonia has been demonstrated to power automobiles, space heating, process heating, electricity generation, and even experimental military aircraft (see Illustration 3). Pure NH_3 can be used to fuel spark-ignition engines and fuel cells with operating temperatures over 350 ºC. A mixture of 95% NH_3 + 5% diesel can fuel diesel engines. Burners can use 95% NH_3 + 5% H_2, the H_2 being generated from the NH_3 by an in-line reformer. Low temperature fuel cells can also use an in-line reformer to utilize NH_3 as a H_2 storage medium. In all cases, the emission products from NH_3 fuel are N_2 and H_2O. Traces of

NO_x can be produced if NH_3 is used in high temperature, high pressure combustion processes, but that is the case with any fuel that uses atmosphere as its oxygen source. It is removed from the exhaust with a catalytic converter. [1]


Illustration 3: An X-15 experimental airplane powered by ammonia.

Ammonia Synthesis Methods

NH_3 is presently made by the Haber-Bosch process, which involves multiple stages of reacting N_2 and H_2 at moderate temperature (300-550 ºC) and high pressure (100-300 bar) in the presence of a modified Fe_3O_4 catalyst. Each stage consumes about 15% of the reactants. The NH_3 reaction is exothermic, so the process gases must be cooled between reaction stages. [7] The reactants for the process are presently obtained by extracting N_2 from the atmosphere using air separation units and by extracting H_2 from natural gas using a steam reforming reaction. Using those processes, ammonia production requires about 9,500 kWh/ton of NH_3 produced [9], and the NH_3 sells for about the same price as gasoline on a stored energy basis. [1] “Green” Haber-Bosch NH_3 using electrolyzers to to make hydrogen will cost more because electrolysis takes more energy than steam reforming. It is estimated that the energy requirement for a green Haber-Bosch process is 12,000 kWh/ton of NH_3 produced. [8]

A more energy efficient method of producing NH_3 is “solid state ammonia synthesis”, or SSAS. This process removes the need for water splitting, which reduces the energy usage to about 7,500 kWh/ton of NH_3 produced. In solid state ammonia synthesis, a proton-conducting membrane is heated to about 550 ºC. Nitrogen is admitted to one side of the membrane and water vapor is admitted to the other side, as shown in Illustration 4. The gas phase H_2O dissociates into protons and oxygen, an external voltage drives the protons through the membrane, and the nitrogen and protons react on the nitrogen side of the membrane to form NH_3. [8] The lower energy consumption of the solid state ammonia synthesis process suggests that it will be able to produce ammonia at a lower cost than the Haber-Bosch process. Solid state ammonia synthesis may also be more amenable to the variable production rates required to work well with wind or solar power than the Haber-Bosch process is.

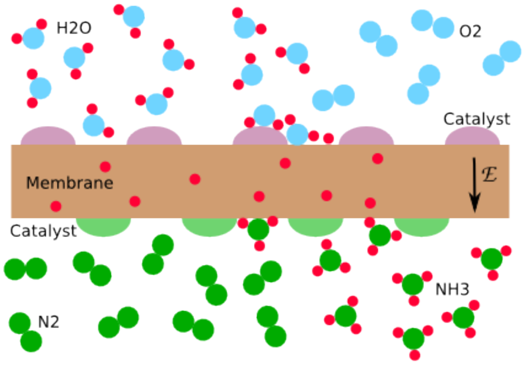

Illustration 4: A schematic depiction of the SSAS process. The electric field is supplied by an external source.

The key processes in solid state ammonia synthesis are: 1) dissociating gaseous H_2O into gaseous O_2 and adsorbed H^+, 2) transporting H^+ through a proton conducting membrane, and 3) reacting H^+ with adsorbed N_2 to make NH_3. Work on solid state ammonia synthesis devices will need to focus on materials that support these processes.

The water dissociation process is the inverse of the hydrogen oxidation reaction in a proton-conducting fuel cell, which suggests that it may be catalyzed by the same catalysts that are normally used in those devices. Platinum, palladium, and ruthenium catalysts are obvious choices, as well as a variety of other experimental fuel cell and electrolyzer catalysts. Literature reports of solid state ammonia synthesis devices using N_2 and H_2 reactants, as opposed to N_2 and H_2O, have used Ag-Pd paste [11] or porous Pd metal [12] catalysts on the H_2 side of ceramic protonic conductors.

The proton conduction process could, in principle, use any of the proton conducting membranes that have been developed for fuel cells. In practice, the operating temperature of solid state ammonia synthesis devices may need to be high to speed the H_2O dissociation and/or NH_3 formation processes. The specific operating temperature will likely be dictated by the efficiency of the catalysts for those processes. This may restrict the proton conductor to ceramic or high temperature polymer material. There have been literature reports of N_2+H_2 solid state ammonia synthesis devices built with the proton conductors $CaIn_{0.1}Zr_{0.9}O_{3-\alpha}$ [10], $BaCe_{0.90}Sm_{0.10}O_{3-\delta}$ [11], $BaCe_{0.80}Gd_{0.10}Sm_{0.10}O_{3-\delta}$ [11], $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ [11], and $SrCe_{0.95}Yb_{0.05}O_3$. [12, 13]

The NH_3 formation reaction in solid state ammonia synthesis is similar to what occurs in the Haber-Bosch process, which suggests that the modified Fe_3O_4 catalysts that are used by industry may be suitable for that part of the device. There is an interesting report that an iron catalyst similar to those used commercially exhibited a 13x increase in NH_3 synthesis rate due to Non-faradaic Electrochemical Modification of Catalytic Activity (NEMCA) when joined to a protonic conductor and biased by -1 V in a N_2 + H_2 environment. Although this is not the same configuration as a solid state ammonia synthesis device, it lends credence to the notion that a promoted iron catalyst may work well on the NH_3 side of a solid state ammonia synthesis device. [10] There are also literature reports of alkali-promoted Ru catalysis and nanoparticle Ru catalysis of NH_3 synthesis. [14-18]

Research Needed to Enable Sustainable Ammonia Fuel

There has been relatively little effort put into solid state ammonia synthesis. In the research literature, the few published reports have focused on N_2 and H_2 as reactants, rather than N_2 and H_2O. Reviews of popular literature show only one company, NHThree, that is working on solid state ammonia synthesis. Research in solid state ammonia synthesis is an opportunity for early players to rapidly advance the field.

There is a great deal of effort being put into proton conducting membranes for fuel cell applications, and solid state ammonia synthesis can borrow heavily from that field for membrane development. The catalysts for solid state ammonia synthesis, however, need research and development efforts focused on the specific needs of the device. From a technology development standpoint, we need researchers to start making N_2 + H_2O solid state ammonia synthesis devices with fuel cell membrane materials so they can 1) use them to study the effectiveness of different water dissociation and ammonia production catalysts, and 2) learn more about the overall functioning of N_2 + H_2O solid state ammonia synthesis devices.

The Renewable Energy Materials Research Science and Engineering Center and the Colorado Fuel Cell Center at Colorado School of Mines have world class efforts in developing both ceramic and polymer proton conducting membranes for fuel cells. This makes CSM an ideal place to start a solid state ammonia synthesis program. Initial efforts would use both ceramic and polymer membranes to make solid state ammonia synthesis devices using Pt and/or Pd to catalyze water dissociation and modified Fe_3O_4 and/or Ru to catalyze ammonia synthesis. Results from that basic work will provide the first research literature data on the functioning of N_2 + H_2O solid state ammonia synthesis devices and will provide essential baseline performance information to guide subsequent research.

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