AMMONIA AS A FUEL

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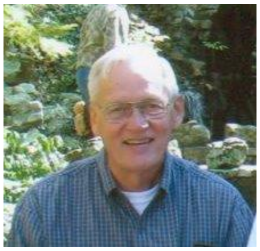

Anhydrous ammonia (ammonia without water) can be a substitute for petroleum as a transportation or power generation fuel. Combustion of ammonia yields water and nitrogen. Ammonia is manufactured using heat and pressure, and the heat and pressure can come from almost any energy source, so production can use the cheapest, cleanest and/or greenest source. Ammonia can be used in internal combustion engines with minor modifications. It can be used in gas turbines, and improved ammonia fuel cells are being developed. Substantial ammonia distribution infrastructure already exists in the Midwest, mostly for the fertilizer industry. In addition, existing fuel dispensing infrastructure can be converted to ammonia. Safety issues with ammonia are no more severe than those with gasoline and diesel fuel. (See “Ammonia as a Transportation Fuel,” AgMRC Renewable Energy Newsletter, May 2009, by *Don Hofstrand,* https://www.agmrc.org/renewable-energy/renewable-energy-climate-change-report/renewable-energy-climate-change-report/may-2009-newsletter/ammonia-as-a-transportation-fuel)

Background - An ammonia molecule is composed of one atom of nitrogen and three atoms of hydrogen (NH_3). Most of the ammonia in the environment comes from the natural breakdown of manure and dead plants and animals. When ammonia combusts it produces nitrogen (N_2) and water vapor (H_2O). Similar to propane or liquid petroleum gas (LPG), ammonia is a gas at normal temperature and atmospheric pressure but a liquid at higher pressures (about 150 psi at 75 degrees F). It can be stored and transported as a liquid but used as a gas.

Both gasoline and diesel engines can be converted to run on ammonia. The first utilization of liquid anhydrous ammonia as a fuel for motor-buses took place in Belgium in 1943 when diesel fuel was scarce. The motor-bus fleet went thousands of miles on a mixture of ammonia with a small amount of coal gas during WWII.

In the 1960s, NASA's X-15 rocket-powered airplane used liquid ammonia and liquid oxygen, and achieved a world record for the highest manned flight Mach number of 6.7.

Ammonia has not been pursued as a fuel for combustion systems for many years, but has been researched to improve the technology. The 1990s saw renewed interest in the utilization of ammonia as an energy source to address global warming, and research into using ammonia for reciprocating engines and gas turbines has resumed.

Ammonia has a high octane rating (about 120), so it does not need an octane enhancer and can be used in high compression engines. However, it has a relatively low energy density per gallon. It’s about half that of gasoline, so, in a vehicle, the fuel mileage of ammonia is about half that of gasoline. As with hydrogen, ammonia has no carbon emission when combusted because it doesn’t contain carbon. In internal combustion engines, ammonia needs very high pressures to compression ignite, so a small amount of another fuel such as hydrogen, LNG, diesel or biodiesel must be used in diesel engines.

Since WWII, research on ammonia engines has come in fits and starts, even as ammonia supplies soared. In the 1930s, worldwide annual production of ammonia was about 300,000 metric tons. Today, the world produces about 150 million metric tons of ammonia every year, but the transportation sector has had little incentive to use it since petroleum has a higher energy density and is easier and cheaper to produce.

Half of the hydrogen produced in the chemical industry is used for ammonia production. In addition to ammonia, hydrogen can be stored in other light chemicals such as methanol and ethanol. Ammonia has an advantage over those in that it does not contain carbon and will not release CO_2 when used as fuel. It is much less expensive to produce, store, and deliver hydrogen as ammonia rather than as compressed and/or liquid hydrogen.

Ammonia and fuel cells – https://www.frontiersin.org/articles/10.3389/fenrg.2014.00035/full, “Ammonia as a suitable fuel for fuel cells,” by Rong Lan and Shanwen Tao, University of Strathclyde, Glasgow, UK advocates the use of ammonia in fuel cells.

Ammonia can be used in fuel cells, but we more often hear that hydrogen is our ultimate renewable and green fuel source. Hydrogen fuel cells take in hydrogen (H_2) and oxygen (O_2), produce electrical power, and emit water

(H_2O). Hydrogen is the most abundant element in the world but it is relatively rare in its elemental (H_2) form. Although hydrogen has high energy density by weight, it is the lightest of all elements and requires large volumes for motor vehicles or power generation. Hydrogen is difficult to store and transport. Hydrogen can be compressed as either a compressed gas or liquid hydrogen, but the pressures required to do either are substantial and create a potential safety hazard.

Ammonia is sometimes called the “other hydrogen” due to its high content of three hydrogen atoms in a molecule of ammonia. The ability of ammonia gas to become a liquid at low pressures means that it is a good “carrier” of hydrogen. Liquid ammonia contains more hydrogen by volume than liquid hydrogen, and is over 50% more energy dense per gallon. Since ammonia can be stored and distributed much easier than hydrogen, fueling stations are much easier to convert to dispensing ammonia rather than hydrogen.

To use ammonia with a hydrogen fuel cell, it is necessary to separate the ammonia into its hydrogen and nitrogen elements before it is used. Alternatively, there are several fuel cells designed to use ammonia directly, enabling high efficiency conversion of ammonia to electric power.

Safety - Ammonia is safer than propane and comparable to the safety of gasoline when used as a transportation fuel. Ammonia vapors cause irritation to humans at low concentrations and is life threatening at high concentrations. However, ammonia can easily be detected by its strong odor. It is lighter than air and rapidly dissipates in the atmosphere. Regardless, safety precautions need to be implemented for handling ammonia.

Unfortunately, when burned at high temperatures, ammonia produces nitrogen dioxide, which contributes to smog and acid rain. Combustion also yields some nitrous oxide—a greenhouse gas that's significantly more potent than CO_2 and methane. But technologies such as selective catalytic reduction can be used to avoid these.

In some respects, ammonia is safer than gasoline. Gasoline vapors are carcinogenic but ammonia vapors are not. Ammonia does not burn readily or sustain combustion except with fuel-to-air mixtures of 15-25% air. Explosions and fire are less likely with a ruptured ammonia tank than with gasoline. Also, gasoline can produce hazardous carbon soot particles, but ammonia contains no carbon and does not produce soot.

Ammonia production and distribution - Currently ammonia is primarily produced from natural gas and coal. China is the number one producer. In the U.S., ammonia is made primarily from natural gas. Hydrogen is taken from the natural gas and nitrogen comes from the atmosphere. Although ammonia used in the U.S. has traditionally been produced domestically, imports of ammonia have increased substantially in recent years.

Although ammonia does not produce CO_2 during combustion, the production of ammonia from natural gas does emit CO_2. Carbon sequestration at the point of production could greatly reduce these emissions.

Better yet, instead of using fossil fuels, ammonia can be produced using a renewable energy source. For example, electricity from wind energy can be used to create hydrogen through the electrolysis of water into hydrogen and oxygen. The electricity could also be produced from solar energy, nuclear power, geothermal energy, ocean and tidal energy and others.

Carl Bosch (chemical engineer) Fritz Haber (chemist)

Regardless of the energy source for the hydrogen, nitrogen is taken from the atmosphere (78% of earth’s atmosphere is nitrogen) and hydrogen and nitrogen are converted to ammonia through the Haber-Bosch process, which was invented over 100 years ago by F. Haber and C. Bosch. The process uses an iron-based catalyst at high pressure (100–300 atmospheres) and high temperature (750–930°F) to combine hydrogen and nitrogen.

Prior to the 20th century, the most common fertilizer used to grow food was manure. And one of the most important sources of that manure was bird and bat guano, which was found in remote tropical locations. With the global population rapidly expanding at the beginning of the 20th century, it became clear the world's guano reserves would not be enough.

Since ammonia can be used as the basic building block to make ammonium nitrate fertilizer, the Haber-Bosch process made it possible to replace manure. More than a century later, this process is still used to make the ammonia for most fertilizers and thus helps feed billions of people around the world. About 90% of all ammonia produced worldwide is used in fertilizer.

Mass production of ammonia began in 1913. In addition to being used for fertilizers, ammonia is also used for chemical raw materials and refrigerants. Even though the Haber-Bosch process is used to produce virtually all of the world's ammonia, it is energy intensive. And since fossil fuels normally provide the energy, it accounts for 1.8 percent of human-caused global CO_2 emissions each year.

The importance of the Haber-Bosch process cannot be overstated. Haber and Bosch were awarded Nobel prizes for their work. For the last 100 years, this process allowed us to have enough food to feed ourselves. It may now keep us from destroying the planet by providing a low-emissions fuel, provided we use renewable fuels for the energy source.

Ammonia is now produced at 32 plants in 17 states and shipped around the country by pipeline, rail, barge, and truck. It is easy to store and deliver in large quantities and is already one of the most transported chemicals worldwide. In addition to the storage and delivery infrastructure that already exists for ammonia, the nearly two million miles of natural gas and petroleum pipelines can be cost-effectively converted to carry ammonia, making it available to nearly every community in the U.S. The ability to use one fuel source, ammonia, in a variety of engines, fuel cells, turbines, etc., is a huge advantage.

A modern ammonia production plant

Biomass Ammonia - Cellulosic ammonia may be more viable than cellulosic ethanol for a fuel. Biomass ammonia from renewable crops such as sweet sorghum (photo) has been shown in Iowa to supply enough hydrogen through anaerobic digestion or thermal gasification to produce a quantity of ammonia that contains more energy per acre than corn ethanol or cellulosic ethanol. Crops like sweet sorghum thrive under drier and warmer conditions than many other crops, so marginal land can be used for energy production.

Energy Storage - Energy produced from most renewable energy sources, such as wind, wave, tidal and solar is typically intermittent, so storage of the energy in batteries, in chemical form, or in some other way, is necessary in order to cushion the effects of fluctuation in energy production. Chemical storage is more economical in comparison to batteries. Ammonia has 10 times the energy density of a lithium-ion battery *and* three times that of compressed hydrogen. Using ammonia for storage also allows for the replacement of fossil-based fuels with carbon-free fuels for use in existing engines or turbines to generate power.

Ammonia is already used as a chemical additive for selective catalytic reduction (SCR) of nitrogen oxides in thermal power generation, and most large-scale thermal power stations have ammonia tanks for that purpose. Since power stations already store, transport and use ammonia, it is a suitable candidate to replace fossil fuels for energy storage with minimal investment.

Producing “Green" Ammonia - Producing “green” ammonia starts with “green” hydrogen. Most commercial production of hydrogen uses “steam methane reforming.” It causes the methane in natural gas to react with steam and releases hydrogen, carbon monoxide, and a small amount of CO_2. That process can be replaced with the electrolysis of water into hydrogen and oxygen using renewable energy. Electricity is also used to cool air to separate the nitrogen from other gases. The hydrogen is then reacted with the nitrogen using the Haber-Bosch process (with renewable energy) to produce ammonia.

Attempts to produce “green ammonia” using “green” hydrogen are beginning on a small scale in several regions:

- A trial plant at the Fukushima Renewable Energy Institute in Japan uses solar power to produce up to 110 lbs of green ammonia a day.
- A demonstration system at the Rutherford Appleton Laboratory in England is powered by a wind turbine and makes up to 66 lbs of green ammonia daily.
- A farmer in Iowa is using solar power to produce green ammonia.
- An inventor from Ontario is producing ammonia from air and water using renewable energy. His small machine takes the excess electricity from wind and solar systems to produce ammonia. When there’s no sun or wind, that ammonia is used in generators.

Larger initiatives are underway in Australia, Chile, and New Zealand. The Australian Renewable Energy Agency recently backed a feasibility project for a plant that could produce 20,000 metric tons of ammonia annually, using 208 gigawatt-hours (GWh) of renewable electricity.

Ammonia and Ships - The shipping industry is a major example of where ammonia could be used as a fuel, and this could result in one of the most significant reductions in our fossil fuel use. Ammonia can be used in existing marine engines. It would have to be produced with renewable sources rather than fossil fuels, and, while there are some pilot projects that do that, scaling up to the necessary volume will be a challenge. With today's technology, the combustion of ammonia is the most effective way to use ammonia as an energy source, rather than fuel cells.
(See https://spectrum.ieee.org/why-the-shipping-industry-is-betting-big-on-ammonia)

Maritime shipping contributes nearly 3% of the world's annual CO_2 emissions, according to the International Maritime Organization (IMO). In 2018, IMO delegates agreed to reduce emissions by 50% from 2008 levels by 2050. A 2020 survey by the American Bureau of Shipping found that two-thirds of shipowners and operators had no decarbonization strategy. Even so, nearly 60% said they view hydrogen and ammonia as the most attractive fuels in the long term. No large vessels today are equipped to use ammonia. Even if they were, the supply of renewable (green) ammonia is virtually nonexistent

Regardless, a handful of projects are moving in that direction:

- Finland's Wärtsilä plans to begin testing ammonia in a marine combustion engine in Stord, Norway.
- Germany's MAN and Samsung are part of an initiative to develop the first ammonia-fueled oil tanker by 2024.
- The supply vessel Viking Energy is being retrofitted with a 2-megawatt ammonia fuel-cell system. Green ammonia will be produced at a plant in Norway.
- MAN is developing an ammonia engine for a medium-size container vessel.

Although other climate-friendly technologies are being considered for shipping (such as fuel cells, hydrogen-storage systems, large battery packs, spinning metal cylinders, and towing kites), it is expected that ammonia will dominate, and some say that nearly all newly built ships will use it by 2044.

For ammonia-fueled shipping to become common, though, ports must build the infrastructure to handle ammonia, and large investments in renewable-energy must be made to produce enough green ammonia for thousands of ships. The global shipping industry used the power equivalent of 3.05 million GWh in 2015. Producing green ammonia for all ships would take 5.5 million GWh of renewable electricity, according to the Korean Register of Shipping.

Fortunately, operators of chemical tankers already have experience handling ammonia. In addition to ammonia tankers, since the properties of ammonia are similar to propane, ships that transport propane can generally be used for ammonia.

To improve ignition, ammonia can be combined with diesel fuel, though that would not completely eliminate the ship's carbon footprint. But shipbuilders can use technologies like selective catalytic reduction to greatly reduce greenhouse gases.

Fuel cells do not have harmful emissions since they do not burn fuel. Unfortunately, existing fuel cells don't have adequate power for large ships, but experts believe they will eventually have a higher efficiency than internal combustion engines. A big container ship would need more than 60 MW of fuel-cell capacity

There have been a number of *hydrogen* fuel cells used in smaller vessels, and they could use ammonia as a source for the hydrogen. However, a "solid-oxide fuel cell," can use ammonia directly. This is what is being installed on the *Viking Energy* supply ship. And the Swiss line MSC Cruises is having a new vessel built with a 50-kW solid-oxide fuel cell system.