



Ammonia and Biofuels

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The following is a guest post by Dave Bradley ([TOD User: nb41](#)), who has some very good technical essays on wind power (as well as his contact info) [here](#). Dave introduced himself to me via e-mail several months ago, and after exchanging a few e-mails in which we covered many technical issues, it became clear that we share a number of very similar interests. One of Dave's essays that caught my attention involved the very interesting idea of using excess wind power to make methanol, ethanol, or even ammonium nitrate fertilizer. But Dave doesn't just throw an idea out there; he gets into the important technical details. I first mentioned Dave's paper in my essay on [Compressed Air Energy Storage](#).

Dave explains in the following essay how we could use renewable energy to make nitrogen fertilizer, thus taking some of the fossil fuel inputs out of biofuels production. By doing so, the energy return would be substantially improved, which is one thing that must happen before biofuels can be truly sustainable. So, it is my pleasure to present Dave Bradley's ideas for helping to mitigate our energy problems.

Ammonia and Biofuels

Since biofuels (and right now ethanol, alias EtOH) are the subject of some controversy regarding the composition of fuel blends used in transportation, many arguments invoke the "ammonia problem". As our country is currently arranged, almost all ammonia (=NH_3) produced or imported is partly derived from natural gas, although the high price and higher probable future price are going to bring coal into the ammonia equation. NH_3 or its many derivatives (and "natural" forms, like manure) are essential for high productivity agriculture, especially as defined and practiced in the U.S. It also is how plants manufacture amino acids/proteins; after all, there is no nitrogen in molecules like glucose, fructose, sucrose, starch and cellulose. My interest is in getting the "non-renewables" out of renewable energy (and fuels in particular) as much as possible, and this semi-torrent of misinformation on NH_3 is somewhat frustrating, so maybe this effort will lead to a more informed discussion.

The nitrogen molecule is very stable; one of its primary uses is as an "inerting gas" (ever knit a nitrogen blanket?). I have used N_2 as an inerting/diluent for fluorine, so that is a good measure of the stability of the N_2 molecule. To become useful to plants, the N_2 molecule must be either oxidized with oxygen (making nitrites and nitrates) or reduced with, in some way, hydrogen, which can then be used in a myriad of routes. In nature, elemental nitrogen is oxidized by lightning, while reduction (to ammonia and other forms) occurs as a result of some bacterial action on either elemental or oxidized nitrogen. Other bacteria take reduced nitrogen (amines, amides, ammonia) and oxidize it to nitrites/nitrates, which are then reduced to elemental nitrogen (and in the process used as a source of oxygen) by other bacteria, and thus keeping a balance in nature.

There are some crops (notably, beans) which can nurture nitrogen fixing bacteria around their roots, but the production rate of these bacteria is insufficient to supply the plant with enough nitrogen at high productivity levels; after all, soybean production consumes a lot of nitrogen based fertilizers.

The N_2 molecule reduction occurs when a catalyst coordinates with the triple bond, and this lowers the activation energy for reactions. N_2 reduction by H_2 molecules is actually a fairly exothermic reaction (-10.96 kcal/gm-mole), or about 1161 Btu liberated per lb formed. In other words, a bit more than one pound of steam can be made for each pound of NH_3 made. NH_3 has been produced industrially at large scale since the invention of the Haber Process, where the use of an alkali promoted iron sponge catalyzed the reaction of N_2 and H_2 at high pressures (200 + atmospheres) and elevated temperatures. This ends up being an equilibrium process, where the extent of conversion of N_2 is determined by the temperature, pressure and mole ratios in the reaction zone. With the iron sponge system, conversions per pass are a bit more than 17 %; after separating out the ammonia, the unreacted N_2 and H_2 are sent back to the reactor. Separating out the ammonia involves stepping down from the supercritical (for NH_3) conditions. Thus, producing NH_3 from the two elements might involve a lot of energy, but clever engineering can cut this down considerably (for example, using turbines to depressurize the reaction mixture, recovering a considerable quantity of energy that can be used for compressing N_2 and H_2 to reacting conditions).

Better catalysts have been developed to improve the per-pass conversion, such as those used in the KAPP system. Nowadays, a combination of the KOH-activated iron sponge (initial catalyst) and ruthenium (similar to iron, but 4d instead of 3d on the periodic table) now are used to achieve about 25% per-pass conversion. In addition, due to the heat liberated by the reaction/need for temperature control (at around 500 F), steam cogeneration can be employed to take the reaction energy and use it to (at least partially) drive the enormous gas compressors needed in industrial scale processors. Obviously, catalyst poisoning is highly undesired, so reasonably pure H_2 and N_2 are required for raw material feedstocks. In addition, CO_2 is also an undesired input impurity, as this would lead to urea and other complications, "gumming up the works". Obviously, O_2 would just consume H_2 , further wasting time and effort.

As originally practiced, the N_2 for the Haber Process was readily obtained by cryogenic air distillation. The H_2 could be obtained by electrolysis of water, which would make very pure H_2 high quality feed with relative ease. This process was extensively practiced in Norway by Norsk Hydro (and its predecessors), and was also used in North America (for example, at Trail, British Columbia, on the Columbia River, 15 miles north of the border) by Airco (now BOC). The H_2 could also be made by the water gas reaction using coal or petroleum, but the resulting syn-gas had to be extensively cleaned up of ash, sulfur, arsenic, CO, CO_2 , and other chemical "varmints". In fact, the H_2 purification part of the site would be one of the largest and most expensive parts of an NH_3 plant.

As the 20th century rolled on, methane became the H_2 source of choice, as it was really cheap, readily available and easy to use compared to coal. The water gas reaction is endothermic, so energy must be supplied in the form of steam (water feed) and just plain heat to drive the reaction; carbon is removed eventually as CO and/or CO_2 , and any CO can be readily oxidized to provide more energy for this process. In other words, preparing NH_3 from CH_4 also involves the co-production of CO_2 . Thus, using natural gas as a feedstock for NH_3 production does contribute to global warming, especially considering the volumes of NH_3 produced. Obviously, coal use for NH_3 synthesis sends us to the proverbial "Big Fryer Down Below" at a faster rate, environmentally speaking. But in general, people will say they care about future generations, but

rarely do anything about their utterances, such as pay higher energy taxes. You know, the "fertilizer walks" saying.

Up until the Crooked E (Enron) started doing its organized and unorganized criminal run on California, most NH_3 was priced around \$100/ton. Nowadays it is around \$450/ton, and a considerable amount of U.S. NH_3 production has been shut down. We now import a lot of NH_3 from places like Trinidad, which have more N gas than they can readily consume, and cheap local N gas prices. However, these high prices are providing a hint of where future, non-polluting NH_3 can be made - from wind turbines. In fact, using any H_2 made in large scale from wind turbine derived electricity for NH_3 synthesis may prove much smarter than using this H_2 as boiler fuel or for transport in SS 304 pipelines to cities. In some ways, this is a perfect match of a vast wind resource (on the Great Plains) with vast farming regions. Sending electricity in bulk to metropolitan areas will not leave a lot of that created value (from wind turbines on farmland) on the farm. So the use of this electricity to make NH_3 , like EtOH preparation from relatively worthless (money-wise) crops like corn, could be viewed as adding value to an otherwise cheap commodity for rural communities.

Anyway, at one time in the recent past, NH_3 consumption on the farm was about 12 million/tons/yr, out of 14 million tons/yr produced. To make all 14 million tons/yr of NH_3 , about 2.47 million tons/yr of H_2 must be prepared and purified (or just prepared and dried in the case of electrolysis). To make 1 ton of H_2 using industrial scale electrolysis units requires about 45 MW-hr. So, if electrolysis units operate at 8700 hr/yr, a steady rate of about 72.5 GW of electricity would be needed, requiring 194 GW of wind turbine capacity, or 77,600 x 2.5 MW wind turbines operating at an average capacity of 37.5 % to make all the H_2 needed to make all the NH_3 used in the USA.

And the last statistics - corn growing uses about 40% of U.S. ammonia fertilizer, while soybean production uses about 6%. These crops use up about 6 million tons of NH_3 per year. And most of that ends up going out the "exhaust ports" of cows, pigs and chickens.....and never ends up being consumed as food by the human carnivores who (in general) manufacture the cows, pigs, and chickens via factory farming/feedlots. A strange world, and not a pretty one with regards to how that part of the US food supply is concerned, so if you don't like it ugly, don't look at it too closely.

So, some big questions on this topic could be:

What price Global Meltdown?

Is there room in the Midwest for 77,600 turbines (each one occupies about 1/16 acre for the (largely) buried foundation)?

What is 5% of U.S. N gas consumption worth, especially 10 years from now?

And the view....how can we compensate some people for the grief of actually observing how some of their energy is produced?

Meanwhile, back to the EtOH energy balance for a minute. In theory, a corn farm uses about 1500 Btu/gallon of EtOH for electricity on the farm, and about 7500 Btu/gal EtOH for the NH_3 consumed. The electricity used on the farm that could be made from non-renewables such as coal, N gas and nukes also could be made from wind turbines, especially in the Great Plains/Great Lakes area. But the H_2 preparation for NH_3 synthesis will not be changed until fossil fuel prices rise, and the external costs of this fossil fuel consumption are reflected in the price. And the same goes for other N gas consuming activities. On a raw material basis, the breakeven point is for a

delivered price of natural gas at \$11.60/MBtu (not Henry Hub!) and wind turbine electricity at 5 c/kw-hr delivered.

Meanwhile, the electricity consumption of a corn to EtOH facility is about 1.2 kw-hr/gallon of EtOH produced (with CO₂ recovery), less if it is vented off (CO₂ compression uses about 185 kw-hr/ton recovered). Each billion gallons made uses an average of about 160 MW. Lets say we get up to 10 billion gallons/yr in the near future. Powering up these plants with non-polluting electricity would only require about 4300 of these same wind turbines. But on the accounting end of things, if this electricity were directed in this manner to EtOH plants, a significant reduction in the amount of non-renewable energy used to make EtOH would be the result. However, according to some, this is just an accounting trick. And again, putting more renewable in renewable fuels won't happen until it gets more expensive to use fossil fuels for such processes, and also more expensive to pollute our atmosphere with excess CO₂, which is roughly equal to the quantity of anthropogenic CO₂ made these days (remember the Frog Boiling article on TOD?). And given today's stilted economics, also something not likely to happen in the near future until energy prices are "re-prioritized".

Your thoughts.....



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