The Historical Development and Significance of the Haber Bosch Process

By David E. Kissel

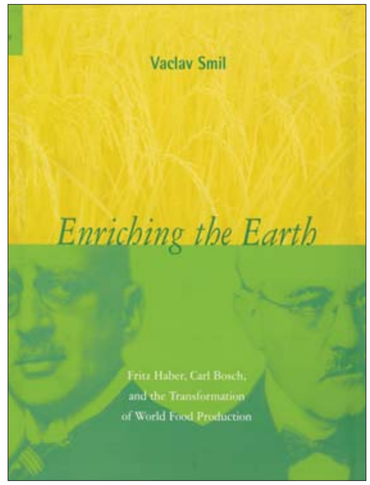
A review of key scientific discoveries in the mid 1800s on the role of N in crop production, and the later research in the early 20th century of scientists Fritz Haber and Carl Bosch that made N fertilizer production possible. Dr. Kissel draws from several sources for this historical assessment that links N supply with social change and security—especially from the book by Vaclav Smil entitled "Enriching the Earth" as well as "The Alchemy of Air" by Thomas Hager.

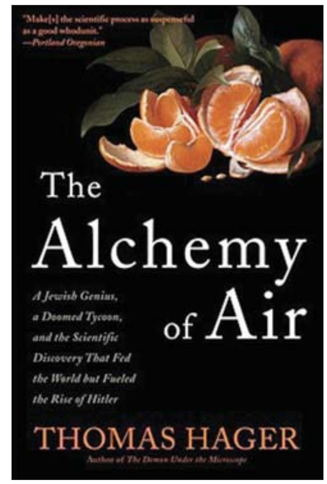
Today we in agriculture take for granted the importance of the production and ready availability of N fertilizer. But around 175 years ago, a group of scientists in Europe were involved in a scientific debate over how important ammonium and nitrate forms of N were for the growth of plants, and whether N fertilizers were needed at all. By 1836, the French chemist Jean-Baptiste Boussingault had summarized field experiments on manuring, crop rotation, and sources of N. He concluded that N was a major component of plants. An important question in 1840 was whether plants could get all of the N they needed from the soil and from the air. The great German chemist Justus von Liebig had concluded that soil and atmospheric ammonia supplied enough N for the needs of crops, but this conclusion was wrong. Scientists at the time who found the right answer to these questions were John Bennet Lawes and Joseph Henry Gilbert, who showed clearly at Rothamsted, England that addition of N fertilizers greatly increased yields of wheat. Why the great scientific interest in N during the 1800s? Besides the scientific curiosity to understand plant growth and plant nutritional needs, there was also the need to ensure food supplies for an expanding population.

In his book, Smil describes the doubling of wheat yields in England from 1750 to 1850, which he concluded was due to crop rotations that included more legumes, which in turn supplied more N to the following wheat crop. He noted that during the 500 years prior to 1740, legume use in the county of Norfolk, England was relatively constant at 13% of cropped land area whereas by 1836 it had doubled to 27%. Smil quoted from historian G.P.H. Chorley of the University College in London, who wrote about the importance of more legume use to industrialization during this period. Chorley's article, published in the journal Economic History in 1981 was titled "The Agricultural Revolution in Northern Europe 1752 to 1880: Nitrogen, Legumes, and Crop Productivity." Chorley concluded "*…there was one big change of overriding importance; legume crops and the consequent increase in the N supply. It is not fanciful to suggest that this neglected innovation was of comparable significance to steam power in the economic development of Europe in the period of industrialization.*" Smil wrote that Chorley did not exaggerate; he stated "*Industrialization would not have been possible without population growth. A higher N supply allowed not only more people per unit of arable land, but also for the slow but steady improvement of average diets.*"

Less than 50 years after the questions about N were settled by Lawes and Gilbert there were new questions and controversies over how the growing population of the industrialized

Abbreviations and Notes: N = nitrogen; M = million.





nations were going to feed themselves in the coming 20th century. At the end of the 1800s, Great Britain was importing much of its wheat. In an 1898 speech widely quoted in the popular press, William Crooks, the incoming president of the British Association for the Advancement of Science, made a case that "Industrialized Nations" must find a solution to the coming food shortage. He called for chemistry research to find a solution; hopefully, a scientific breakthrough that would allow the manufacture of N fertilizers.

The solution was to come first from the young German Physical Chemist Fritz Haber. Haber graduated in 1891 with a doctorate in chemistry. While employed by the University in Karlsruhe, Germany, Haber wrote many papers including one in 1905 in which he concluded that the chemical reaction of N and hydrogen gases to produce ammonia was not feasible, largely because the yields of ammonia in his experiments were too small. But another chemist, Walter Nernst, challenged Haber's work as incorrect. The public criticism drove Haber, with financial support from BASF, to restart the work on ammonia synthesis in order to clear his name. By March 1909 Haber and his colleagues, through much trial and error, had found the right combination of high temperature (500°C) and pressure (100 atmospheres) and just the right catalyst to show that the reaction could be successful. In July 1909, BASF assigned Carl Bosch to lead the team to develop commercial scale production.

Industrialization was not easy. Ammonia production was to be a continuous flow process at the extreme temperatures and pressures defined by Haber's work. Chemical production prior to this time had been done in batches, unlike what was being proposed. This meant that almost all of the machinery had to be invented for these extreme conditions, including flow gauges, pressure gauges, etc. that could withstand these

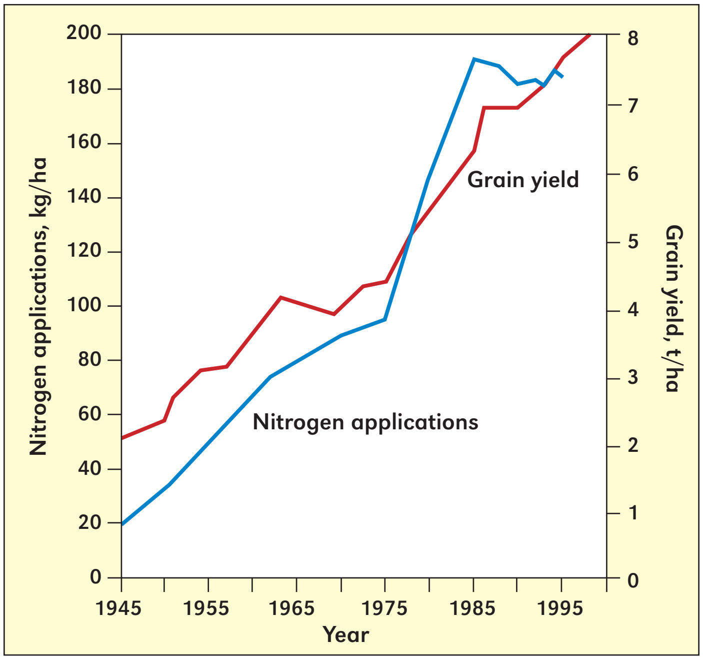


Figure 1. Nitrogen applications and yields of English winter wheat, 1945-1998. Source: Smil, 2001.

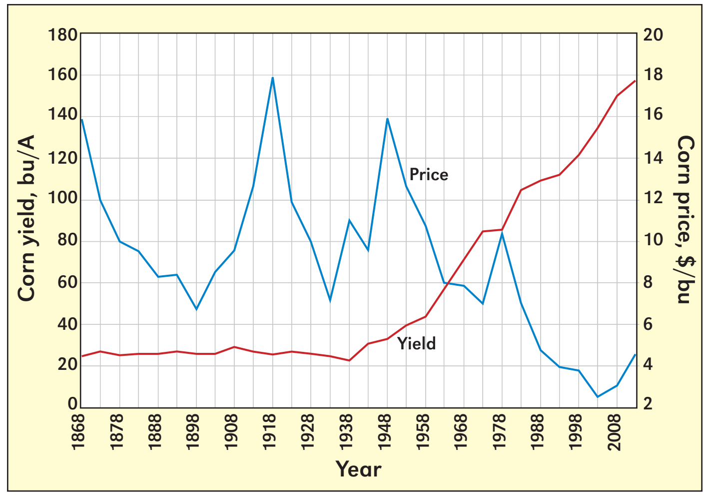


Figure 2. U.S. corn yields and price of corn (per bushel) normalized to the 2010-dollar value. Source: USDA ERS.

extreme conditions. Haber's lab-scale machine that produced 115 g of ammonia per hour was first duplicated by Bosch in the form of a 8 m tall industrial reactor at Oppau, Germany that produced 90 kg of ammonia per hour and the plant began full production in early 1914.

Shortly thereafter, WWI began and the plant soon installed the capability to produce nitric acid from ammonia, which greatly facilitated the manufacture of explosives for the war effort. According to both Smil and Hager, the invention of ammonia synthesis for agriculture greatly lengthened WWI because it could readily be used to make explosives. After the war, the German government at first attempted to keep secret the process for making ammonia, but in negotiations at Versailles to discuss reparations for WWI, Carl Bosch (a member of the negotiating team from Germany) offered to the French government the technical details to build a Haber-Bosch plant. By the early 1920s, the French were producing ammonia, and the British and the Americans soon followed with their own plants.

Two Nobel Prizes were awarded for this work, the first to Fritz Haber, presented in 1920 for his laboratory research describing the conditions needed to form ammonia from N and hydrogen gases. The second, given in 1932, was shared by Bosch and Frederick Bergius for "their services in originating and developing chemical high-pressure methods."

Today's modern ammonia plant is large, often producing over 1,000 tons per day. It takes about 0.65 tons of natural gas to make 1 ton of ammonia. The overall reaction is highly efficient, in part because about 40% of the hydrogen comes from water in the overall reaction. The N of course is from the air.

Haber Bosch has greatly increased yields of food and feed grain crops. Smil presented the changes in yields of wheat in England from 1945, when they were about 2 t/ha (30 bu/A), to 1998 when wheat yields were over 8 t/ha (120 bu/A) (**Figure 1**). The gradual increase in yields over this time were in parallel with the increase in N fertilizer application from about 20 lb N/A in 1945 to about 160 lb N/A in 1998. Corn grain in the U.S. is a similar story. Average yields of corn in the U.S. from 1868 until the present time are shown in **Figure 2**. Grain yield of about 25 bu/A changed little over the 70-year period from 1868 to 1938. After that time yields began to increase slowly, but then increased at a faster rate from about 1960 until the present time. No doubt the introduction of hybrid corn in the 1930s had a significant role. But the big factor, as with wheat production in England was N fertilizer use. Average yields increased at a modest and continuous rate from the early 40s until 1960, as did N fertilizer use. Nitrogen fertilizer use increased at a faster rate starting around 1960 and so did corn yields.

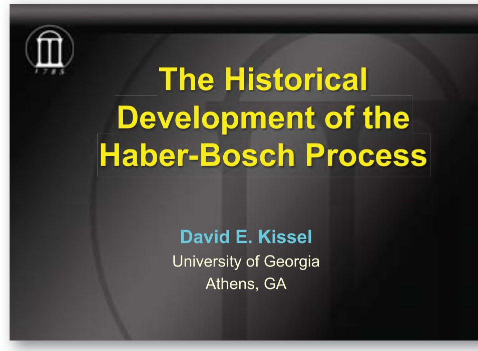
As described by Smil, a big change in ammonia manufacturing plants began to take place in the 1960s. The energy used to make ammonia in the new ammonia plants in 1970 was only 65% of what it had been 15 years earlier and less than half of pre-World War II plants. This allowed exceptionally low retail prices for ammonia at that time, for example in 1969 it was possible to purchase anhydrous ammonia for $0.04/lb of N. With low prices for N fertilizer and a relatively good price for corn, yields increased continuously over the next 30 years. By 2010 average yields were nearly 160 bu/A, which is more than a six-fold increase in yield in a period of 70 years. **Figure 2** also compares corn yield with the price of corn normalized to the 2010-dollar value. The low point on the graph around 2003 was around US$2.50/bu. The market price of corn has been trending downward from 1948 until 2005 with only one significant price increase around 1978. A similar price drop over this time also occurred for wheat and rice. Of course the effect of greatly increased N supply, the efficiencies of production due to N fertilizer, and all the other factors of production (plant breeding, pest control, mechanization, irrigation, and other plant nutrients) have all made the higher yields and increased efficiencies of production possible. The net result of all these improvements is a reduced price, which has had a big effect throughout the economy. For example in 1930 nearly 25% of U.S. family income was spent on food, but this percentage has dropped over the intervening 75 years to less than 10% today, which allows a higher standard of living.

In some respects N has become overly abundant. Fertilizer manufacture each year is 100 M tons, modern legumes like soybeans and alfalfa contribute another 40 M, and burning of fossil fuels an additional 20 M. This total of 160 M tons is about 55 to 60% of all N fixed each year. In other words humans have more than doubled the amount of N fixation in the past 100 years. And, much of this fixed N is concentrated on our best agricultural land in an environment where N may be lost by nitrate leaching, some of which may reach the marine environment and cause eutrophication. Ammonia volatilization from fertilizers and animal manures may also cause eutrophication and soil acidification. Finally some N may be lost as nitrous oxide by denitrification and nitrification; and nitrous oxide is a strong greenhouse gas.

But we cannot do without N fertilizer. The central challenge is to apply the correct rate of N and in the correct way and at the right time for the crop being grown. This means doing a better job of quantifying some components of the N cycle, perhaps the most important is quantifying the amount of N that becomes available from soil humus and decomposing crop residues in soils because these processes are so complex due to their dependence on environmental conditions. Perhaps better solutions will come from the integration of computer technology, weather data and soil and plant analysis. These challenges should be no greater than those facing Haber and Bosch 100 years ago. BC

Dr. Kissel is Emeritus Professor of Soil Science, University of Georgia; e-mail: dkissel@uga.edu.

The article is a summary of the 2011 Distinguished Leo Walsh Lecture presented by Dr. David E. Kissel at the annual meetings of the Soil Science Society of America in San Antonio, Texas. The recorded lecture may be found at ACSESS Digital Library (2013).



A complete version of Dr. Kissel's presentation can also be obtained at http://www.ipni.net/article/IPNI-3359

References

ACSESS Digital Library. 2013. 2011 Leo M. Walsh Soil Fertility Distinguished Lectureship, D.E. Kissel. https://dl.sciencesocieties.org/publications/meetings/2011am/8794 Verified November 8, 2013.

Hager, T. 2008. The Alchemy of Air. Harmony Books, NY, USA.

Smil, V. 2001. Enriching the Earth. MIT Press, MA, USA.

Examples of N response taken from the U.S. spanning the mid 1930s to mid 1950s. Better Crops with Plant Food Cover featured in March 1930.