Thesis

"England and all civilized nations stand in deadly peril of not having enough to eat."[1]

Sir William Crookes issued this dire warning at a gathering of England's most esteemed scientists in 1898. Farmers were running out of the nitrogen fertilizer used to feed Europe's expanding population. In 1909, German chemist Fritz Haber unlocked previously inaccessible sources of nitrogen in the air through the Haber process, also called the Haber-Bosch process. Fritz Haber, along with other scientific minds like Carl Bosch and Robert Le Rossignol, invented and industrialized this lifesaving process. His revolutionary breakthrough led to the mass production of nitrogen-based fertilizer which significantly increased global food production.

Nitrogen: Nurturer of Life

Plants need nitrogen to grow. Although nitrogen is plentiful in the air, most plants cannot convert this inert gaseous nitrogen into fixed nitrogen in the soil.[2] Nitrogen intensive crops, like grains, extract nitrogen from the soil faster than it can be replaced.[3] After several harvests, the soil becomes depleted. Natural sources, such as manure and compost, don't contain enough nitrogen for intensive grain farming.[4] Agricultural societies traditionally practiced crop rotation to restore nitrogen and other nutrients to their fields.[5] Europeans grew peas, clover, and beans; the Chinese utilized soybeans, and farmers in the Middle East rotated chickpeas.[6] The secret to the nourishing qualities of beans and legumes lies in special bacteria, like Rhizobium and

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[1] Crookes, WIlliam. *The Wheat Problem*. (London, J. Murray, 1899), 6
[2] Fahad, Shah and Khan Amanullah. *Nitrogen in Agriculture*. (London, IntechOpen, 2018), 96
[3] Smil, Vaclav. *Enriching the Earth*. (Cambridge, MIT Press, 2004), 31
[4] Leigh, G.J. *The World's Greatest Fix: A History of Nitrogen and Agriculture*. (New York, Oxford University Press, 2004), 51
[5] Leigh, *The World's Greatest Fix*, 54
[6] Ibid

Azospirillum, which produce enzymes called nitrogenases that can convert inert nitrogen into fixed nitrogen.[7] However, crop rotation was no longer used by large farms in Europe by the late 1800's.[8]

Post-industrialization, many farms converted to monoculture to supply the population's high demand for wheat .[9] Soil cannot replenish its nutrients fast enough to support growing the same crop repeatedly.[10] Nitrogen was added to the soil through fertilizers, but natural sources of nitrogen fertilizer were nearly depleted.[11] To feed a growing population, more nitrogen was needed. This problem came to the world's attention when Walter Crookes gave a speech at the British Academy of Sciences.[12]

Sir Walter Crookes was a renowned British chemist, discoverer of thallium, and inventor of the Crookes tube.[13] He came to Bristol, England to speak about an imminent world crisis. He declared that crops needed nitrogen to grow, but sources of fixable nitrogen were dwindling.[14] Europe's main source of fixable nitrogen was sodium nitrate mined from Chile,[15] but Crookes predicted that these vast sources of nitrogen would be gone by the 1930's.[16] Crookes warned the

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[7] Smith, Barry E., Raymond L. Richards, and William E. Newton. *Catalysts for Nitrogen Fixation*. (New York, Springer Netherlands, 2004), 23
[8] Hager, Thomas. *The Alchemy of AIr*. (New York, Harmony Books, 2008), 37
[9] Ibid, 63
[10] Fahad and Amanullah, *Nitrogen in Agriculture*, 98
[11] Crookes, *The Wheat Problem*, 42
[12] Hager, *The Alchemy of Air,* 1
[13] Brock, William H. *William Crookes (1832 - 1919) and the Commercialization of Science*. (Oxfordshire, Taylor & Francis, 2008)
[14] Crookes, *The Wheat Problem*, 43. "For years past we have been expending nitrogen at a culpably extravagant rate, heedless of the fact that it is fixed with extreme slowness and difficulty."
[15] Hager, *The Alchemy of Air*, 33
[16] Crookes, *The Wheat Problem*, 42. "If we assume a liberal estimate for nitrate obtained from lower grade deposit, and say that it would equal in quantity that from the richer quality, the supply may last, possibly, fifty years."

crowd, “As mouths multiply, food sources dwindle”; however, if there was a way to take inert nitrogen from the air and break the triple bond that held it, the world could be fed.[17]

Nitrogen and Ammonia Synthesis

A nitrogen atom has three connector points to which other atoms can attach.[18] Nitrogen atoms are reactive and can be used to make essential proteins, amino acids, and DNA.[19] Nitrogen’s reactivity is what makes nitrogen essential to life. When a nitrogen atom bonds with another nitrogen atom, nitrogen gas (N_2) is formed.[20] Gaseous nitrogen is inert, reacting with other gases only at high temperatures.[21] Although this diatomic form of nitrogen makes up 78.09% of the air on Earth, it cannot be used as fertilizer.[22]

To create fertilizer, gaseous nitrogen must be combined with hydrogen to create ammonia.[23]. Nitrogen forms ammonia by linking with three hydrogen atoms. However, methods of combining nitrogen and hydrogen were too inefficient for mass production in 1898.[24] Nitrogen gas is held together with a triple bond, the strongest type of chemical bond.[25] A triple bond is so hard to break that the only thing in nature capable of shattering it, besides certain cyanobacteria,

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[17] Ibid, 45. “The unfulfilled problem, which so far has eluded the strenuous attempts of those who have tried to wrest the secret from nature, differs materially from the other chemical discoveries which are in the air, so to speak, but never matured. The fixation of nitrogen is vital to the progress of civilized humanity.”
[18] Emsley, John. *Nature’s Building Blocks: An A-Z Guide to the Elements*. (New York, Oxford University Press, 2001), 288
[19] Ibid, 289
[20] Ibid, 291
[21] Daintith, John. *Oxford Dictionary of Chemistry*. (New York, Oxford University Press, 2008), 374
[22] Ibid, 375
[23] Hager, *The Alchemy of Air*, 77. “Most of the early efforts focused on machines that would burn the nitrogen out of the air, like lightning did. The mechanical replacement for natural lighting was going to be high energy electric arcs. This approach however, had significant drawbacks - electricity was expensive and this method consumed large amounts of it.”
[24] Ibid, 78
[25] Daintith, *Oxford Dictionary of Chemistry*, 375

is a bolt of lightning.[26] Due to the immense energy required to break the triple bond, ammonia synthesis was a daunting task.

Since 1722, chemists recognized that vast quantities of nitrogen filled the air, inert and inaccessible.[27] Many scientists had attempted to invent a process of artificial nitrogen fixation suitable for mass production, but all had given up when lab accidents, contaminants, and low production obstructed progress to the point of impossibility.[28]Ammonia was the natural choice for a synthetic fertilizer, since it had a simple structure and could be easily implanted into the soil.[29] One such chemist, Wilhelm Otswald, was heralded as the greatest German chemist of his time.[30] He thought he had produced ammonia by putting nitrogen and hydrogen gas under pressure and heating it while running it over an iron catalyst.[31] It was later discovered that ammonia was extracted from contaminants in his reaction chamber, and no ammonia synthesis took place.[32] People looked at Otswald's failure and lamented. If the greatest mind of their generation could not solve this problem, who could?

Fritz Haber and the Haber Process

As a German Jew, Haber faced discrimination in his personal and professional life. He graduated from Karlsruhe University and began his career in electrochemistry in 1891.[33] Despite

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[26] Hager, *The Alchemy of Air*, 68
[27] Emsley, *Nature's Building Blocks*, 290
[28] Hager, *The Alchemy of Air*, 80
[29] Smil, *Enriching the Earth*, 37
[30] Hager, *The Alchemy of Air*, 77. "The shadow of WIlhelm Otswald fell over everything that happened next, and the shadow of Otswald, a giant of science, was substantial."
[31] Charles, Daniel. *Mastermind*. (New York, HaperCollins, 2005), 83
[32] Smil, *Enriching the Earth*, 64. "The small amount of ammonia obtained by Otswald was due not to the fixation of atmospheric nitrogen, but to the hydrogenolysis of iron nitrate formed on the iron catalyst during its treatment before the experiment."
[33] "Nobel Prize Awarded to Prof. Haber". *Denver Jewish News*, February 4, 1920

being an accomplished chemist, he was often passed up for promotions.[34] In 1901 Haber married Clara Immerwahr, the first woman to earn a doctorate in chemistry in Germany.[35] A gregarious but blunt man, he received academic praise and societal condemnation over his development of mustard gas in 1911.[36] Haber's unstable marrage ended when Clara committed suicide in 1915 over strong feelings that Haber's creation of musturd gas was unethical.[37]

Haber's first venture into nitrogen fixation began in 1903 when he received a letter from the Marguiles brothers, owners of Austrian Chemical Works.[38] They requested Haber's help in finding a way to break nitrogen's bonds, thinking it would be very profitable for both Haber and the brothers.[39] Haber refused their offer twice but agreed when the Margulies offered an exorbitant salary.[40]

Artificial nitrogen production is a simple concept. In Haber's own words, "Gaseous nitrogen combines with gaseous hydrogen in simple quantitative proportions to produce gaseous ammonia."[41] Haber postulated that nitrogen gas could be turned into ammonia (NH_3) by breaking nitrogen's triple bond and forcing it to bond with hydrogen by putting both gases under extreme pressure and heat.[42] He first tried to mix nitrogen and hydrogen in a platinum pipe at 1000^{o}C using iron as a catalyst.[43] The reaction caused the gases to bond and create ammonia, but high

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[34] Charles, *Mastermind*, 37
[35] Ibid, 43
[36] Stolzenberg, Dietrich. *Fritz Haber: Chemist, Nobel Laureate, German, Jew*. (Philadelphia, Chemical Heritage Press, 2004.)
[37] Hager, *The Alchemy of Air*, 67
[38] Charles, *Mastermind*, 83
[39] Ibid, 84
[40] Ibid, 84
[41] Haber, Fritz. "The Synthesis of Ammonia From Its Elements." The Nobel Prize Organisation
[42] Haber, Fritz. *Thermodynamics of Technical Gas Reactions*. (Harlow, Longman Greens & Company, 1908), 205. "When we wish to convert nitrogen at all completely into ammonia, we must use a gaseous mixture containing much hydrogen and but little nitrogen."
[43] Charles, *Mastermind*, 85

reaction temperatures burnt up most of the ammonia.[44] Haber could not cool the gases quickly enough to save more than 0.01% of the ammonia created.[45] He seemed to be stuck. High temperatures were needed to produce ammonia, but ammonia evaporated at high temperatures. Such was the problem that prevented many other chemists from achieving artificial nitrogen fixation. Haber reported his failure and moved on.[46]

That might have been the end of Haber's foray into nitrogen fixation if it wasn't for a letter from the renowned chemist Walther Nernst in the fall of 1906.[47] Nerst told Haber that he had repeated his experiment but had replaced some of the heat with pressure and obtained dramatically different results.[48] Nernst concluded that Haber's ammonia yield should have been lower. He planned to publicly correct Haber at a meeting of the Bunsen Society for Applied Physical Chemistry next year.[49] Nernst was a powerful force in German chemistry.[50] Any word from him would trump Haber's. Haber knew this and found the prospect of humiliation unacceptable. He repeated his experiments with new reaction chambers and catalysts.[51] Haber presented his findings alongside Nernst's at the convention in the spring of 1907, even though his results still didn't match Nernst's.[52] Despite this, Nernst dismissed Haber, saying "It is very unfortunate that the equilibrium is more displaced towards the side of very low ammonia formation than the strongly inaccurate figures of Haber had formerly led us to assume, since one

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[44] Ibid, 85
[45] Stolzenberg, *Fritz Haber: Chemist, Nobel Laureate, German, Jew*.
[46] Smil, *Enriching the Earth*, 70
[47] Charles, *Mastermind*, 86
[48] Smil, *Enriching the Earth*, 71. "Nernst's results (obtained at 5MPa and 685^{O}C) showed 0.0032% ammonia yield, only about a quarter of Haber's high value (0.0125%) but close to Nernst's theoretical prediction (0.0045%).
[49] Charles, *Mastermind*, 87
[50] Smil, *Enriching the Earth*, 70. "In 1906 he published his heat theorem, which soon became widely known as the third law of thermodynamics and which earned him a Nobel Prize for physics in 1920."
[51] Charles, *Mastermind*, 86
[52] Ibid, 87

had inferred from them that it might be possible to synthesize ammonia from nitrogen and hydrogen."[53]

Nernst's criticism renewed Haber's determination to finish his work in nitrogen fixation.[54] Haber noticed that Nernst used an air compressor to increase the pressure on the chemical reaction and had obtained slightly more nitrogen than Haber.[55] Haber thought he could use pressure as a partial substitute for heat to prevent the ammonia from evaporating.[56] He obtained a machine that was able to exert 200 atmospheres of pressure, an unheard of number at the time.[57] Haber thought that if he could cool down the ammonia and find a suitable catalyst, he would be able to succeed where Nernst, Otswald, and many others failed.[58] Haber signed a contract with Badische Anilin- & Soda-Fabrik (BASF) in 1907 to fund his efforts.[59] BASF was and still is the most successful organic chemical company in Germany.[60] Like Haber, BASF saw vast profit potential in the nitrogen synthesis industry.

Haber's next problem was to find a way to keep the nitrogen and hydrogen gases circulating inside the chamber while sustaining a pressure of 200 atmospheres.[61] This problem was solved by Robert Le Rossignol, a British chemist and engineer.[62] He created a valve that

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[53] Smil, *Enriching the Earth*, 72.
[54] Charles, *Mastermind*, 87. "Those dismissive words wounded Haber's vanity and stirred up all his insecurities. They drove him like spurs back to the laboratory, and back to the task of capturing nitrogen from the air."
[55] Hager, *The Alchemy of Air*, 90. "Nernst had the right idea, using pressure to push forward the reaction toward ammonia, but had not used enough."
[56] Haber, *The Synthesis of Ammonia from Its Elements*. "To begin with, it was clear that a change to the use of maximum pressure would be advantageous. It would improve the point of equilibrium and probably the rate of reaction as well."
[57] Charles, *Mastermind*, 93. "When Haber replied that the reaction needed 'at least 100 atmospheres', Bernthsen professed shock and disbelief: "Why just yesterday only seven atmosphers blew up one of our autoclaves!"
[58] Haber, *The Synthesis of Ammonia from Its Elements*
[59] Abelshauser, Werner, Wolfgang von Hippel, Jeffrey Allan Johnson, and Raymond G. Stokes. *German Industry and Global Enterprise - BASF: The History of a Company*. (Cambridge, Cambridge University Press, 2003)
[60] Lesch, John E. *The German Chemical Industry in the 20th Century*. (New York, Springer Netherlands, 2013)
[61] Haber, Fritz. *Aus Leben Und Beruf*. (Berlin, Julius Springer, 1927)
[62] Sheppard, Deri. *Robert Le Rossignol: Engineer of the Haber Process*. (New York, Springer Nature, 2019)

could withstand the immense pressure while still allowing gas flow in and out of the reaction chamber. The hot escaping gases also passed heat to incoming gas, thereby cooling ammonia and heating reacting gases, accomplishing a second task in one masterstroke.[63] Haber, immensely pleased, called Le Rossignol "a true engineer."

Haber's last step to achieving nitrogen fixation was finding a catalyst. Haber used his connections in the chemical industry to secure new materials to test as catalysts from Auergesellschaft of Berlin.[64] He spent a year testing dozens of catalysts, but each proved too inefficient. Finally, in March 1909, Haber experimented with the rare earth metal osmium and achieved the breakthrough he desired.[65] Under 200 atmospheres of pressure, the reaction took place at 500^{o}C and broke the triple bond of nitrogen.[66] Nitrogen and hydrogen joined and ammonia flowed. The production was 6% of the total gas mixture, a startling amount.[67] A delighted Haber yelled to his colleagues, "Come on down! You have to see how the ammonia is flowing out!"[68] Haber later delivered his speech *Making Nitrogen Useable* to colleagues at his university.[69] Haber's speech "hit the experts like a bomb."[70] He was soon approached by many individuals who wanted to collaborate. A newspaper later called Haber's discovery "a store of inexhaustible fertility."[71]

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[63] Charles, *Mastermind*, 91
[64] Ibid, 91
[65] Hager, *The Alchemy of Air*, 91
[66] Smil, *Enriching the Earth*, 80
[67] Hager, *The Alchemy of Air*, 92. "The yield was again high - much higher than they had ever seen - high enough to work industrially, high enough to supply the world with fertilizer."
[68] Ibid, 92
[69] Smil, *Enriching the Earth*, 84
[70] Hager, *The Alchemy of AIr*, 108
[71] "Wealth After the War". *The Bridgeport Times*, September 25, 1918. "The Haber process of nitrogen fixation, with its various modifications, is an example of wealth increase by discovery and invention. Here opens a store of inexhaustible fertility; a guarantee that soil cannot fail."

Industrial Production

After Haber's breakthrough, BASF sent chemists Carl Bosch and Alwin Mittasch to Haber's laboratory to determine if his process was viable for commercial use.[72] Carl Bosch, an organic chemist, rose to prominence by discovering the error in Ostwald's botched attempt at nitrogen fixation.[73] Bosch and Mittasch both thought that the Haber process was profitable.[74] Mittash said later he was "deeply impressed and completely convinced" of its potential. Bosch was put in charge of industrializing the process and was given unlimited funding as long as he produced results.[75]

What worked on Haber's small machine did not work on industrial size equipment.[76] Bosch worked alongside Mittasch and a group of engineers to build stronger valves, gauges, and chambers to withstand the pressure and heat of the Haber process.[77] Bosch needed a catalyst that was abundant and inexpensive.[78] Haber had found only two working catalysts: osmium and uranium. However, only one hundred kilograms of osmium was known to exist,[79] and uranium was too expensive and rare to be used as a catalyst. In September 1909, there was a breakthrough. Mittasch had been experimenting with iron catalysts and found that a Scandenavian magnetite worked perfectly.[80] Mineral deposits vary by mine, and Bosch later discovered that calcium and aluminum oxide were what made the catalyst effective.[81] BASF

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[72] Charles, *Mastermind,* 94
[73] Smil, *Enriching the Earth*, 86
[74] Charles, *Mastermind*, 94
[75] Ibid, 96
[76] Smil, *Enriching the Earth*, 85
[77] Ibid, 87
[78] Smil, *Enriching the Earth*, 86
[79] Ibid, 80. "Auergesellschaft used osmium for the filaments of their first metal-filament lamps, and it had accumulated most of the world's total supply, amounting to 100kg."
[80] Hager, *The Alchemy of Air*, 106
[81] Ibid, 107

informed Haber about the breakthrough, and Haber wrote "I am extremely happy that Dr. Bosch and his assistants have succeeded in making such an advance, and I congratulate him and you."[82]

Feeding the World

A commercial plant to mass produce ammonia was constructed in 1913, producing 0.8 metric kilotons in its first year.[83] By 1920, it was producing over 150 times that amount.[84] Other countries quickly adopted this technology despite major technical difficulties in developing machinery capable of mass producing ammonia.[85] In 1916, the US built the Muscle-Shoals plant, their first nitrogen manufacturing plant.[86] BASF overtook the Chilean nitrate industry and became the primary exporter of sodium nitrate.[87] Germany continued to dominate ammonia production,[88] supplying 30% of the global output in 1934.[89] The Haber process drew criticism when a manufacturing plant in Oppau, Germany exploded in 1921 because of technical malfunctions.[90]

Country by country, the world came to rely on the Haber Process as their populations outstripped their natural resources. China faced severe food shortages in 1973 as its population

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[82] Ibid, 108
[83] Smil, *Enriching the Earth*, 242
[84] Ibid, 242
[85] "Nitrate Plant Won't Meet Need." *Bridgeport Evening Farmer*, July 27, 1916. "The Haber process does not make the high demands on electrical power required by the other processes of atmospheric nitrogen fixation in use, but involves technical difficulties in the way of manipulation which have prevented the proportionate extension of its use, even in Germany under present emergencies."
[86] Henry, Thomas R. "Magic Gifts of U.S. Chemists Invaluable to Armed Forces." *Evening Star*. February 9, 1942. "Now American chemical companies can turn out nitrogen by the thousands of tons. Additionally, a chain of government owned plants are now being rushed into production."
[87] Wisniak, Jaime, and Ingrid Garces. "The Rise and Fall of the Salitre (Sodium Nitrate) Industry." *Indian Journal of Chemical Technology*. "Germany's production of synthetic nitrogen compounds, first made on a commercial sale at the beginning of WWI, surpassed that of Chilean nitrate in the early 1930's."
[88] "Nitrogen Supply of U.S. Held Adequate for War." *The Sunday Star*. November 29, 1936
[89] Smil, *Enriching the Earth*, 242
[90] "If This Had Happened About Seven Years Ago." *The Bridgeport Times*, December 13, 1921.

grew to over 800 million.[91] China built five ammonia factories to combat this difficulty.[92] Using nitrogen fertilizer, rice and wheat production doubled and tripled respectively.[93] India and Pakistan went through similar green revolutions during the 1960's when they adopted nitrogen fixation technology.[94] Currently, 76 countries produce nitrogen fertilizer through the Haber process.[95] The Haber process made it possible for many countries to feed their people by providing a cheap, efficient way to fertilize crops.

Haber won the Nobel prize in chemistry in 1918 for his discovery,[96] which has been called the "most far reaching accomplishment in chemical engineering."[97] After Haber's death, German physicist Max von Laue said, *"*Haber will go down in history as the ingenious inventor of the process for combining nitrogen with hydrogen … as the man who by this means won bread from air and achieved a triumph in the service of his nation and all of humanity.*"*[98] This praise is well deserved. Around 40% of global food production is due to the Haber process, and well over half of crops are grown using nitrogen fertilizer.[99] Most estimates state that over half the population could not survive without his work.[100] The Haber process was later heralded as "one of the greatest mileposts in human history."[101]

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[91] Charles, *Mastermind*, 103
[92] Ibid, 104
[93] Ibid, 108
[94] Smil, *Enriching the Earth*, 170
[95] Ibid, 171
[96] "Nobel Prize Awarded to Prof. Haber." *Denver Jewish News*, February 4, 1920.
[97] "U.S. Synthetic Nitrogen May Break Monopoly." *The Sunday Star*. February 14, 1926.
[98] Charles, *Mastermind*, 73
[99] Hager, *The Alchemy of Air*, 89
[100] Smil, *Enriching the Earth*, 35
[101] "Nitrogen Supply Is Now Assured." *The Cadwell Tribune*, May 16, 1924.

Even life-saving inventions can have societal costs. In mass quantities, nitrogen can cause decreased biodiversity, air pollution, and water contamination.[102] Nitrogen fertilizer is used globally, with 82.9 metric tons applied in 1996.[103] Nitrogen is harmful when concentrated in large amounts, particularly in water. Nitrogen runoff from agricultural use can leak into nearby bodies of water, disrupting biodiversity.[104] The nitrate content of the Rhines river rose from 3 ppm in 1940 to 17 ppm in 2000 due to nitrogen runoff.[105] High levels of nitrogen absorb oxygen from the water, creating inhospitable dead zones.[106] Furthermore, only 50% of fertilizer fixes with the soil leading to increased emissions of nitrous oxide, the third most abundant greenhouse gas.[107]

Conclusion

Haber has been credited for "saving the world from eventual starvation."[108] With the invention of the Haber process, Fritz Haber broke the triple bond of nitrogen and solved one of the great scientific problems of his time. Haber and his team used chemistry and engineering to push the boundaries of science to create one of the most impactful, yet least appreciated, scientific discoveries of the 20th century. His work changed modern agriculture and led to the development of cheap, effective fertilizer, which was needed to support the modern world's

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[102] Smil, *Enriching the Earth*, 181. "While the tropospheric concentration of CO_2 has risen about 30% above the preindustrial level, the atmospheric deposition of NO and NH has roughly trebled."
[103] Smil, Vaclav. *Creating the 20th Century: Technical Innovations of 1867-1914 and Their Lasting Impact*. (New York, Oxford University Press, 2005), 104
[104] Sachdev, M. S., Y. P. Abrol, and N. Raghuram. *Agricultural Nitrogen Use and Its Environmental Implications*. (Delhi, I.K International Publishing House Pvt. Limited, 2007)
[105] Smil, *Enriching the Earth*, 190
[106] Sachdev, *Agricultural Nitrogen Use and Its Environmental Implications*
[107] Ibid
[108] Henry, "Magic Gifts of U.S. Chemists Invaluable to Armed Forces." *Evening Star*.

growing population. Haber broke the barriers of nature and science by breaking nitrogen's triple bond and made bread out of air.