The History of Ammonia to 2012

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November 19, 2013

www.tfi.org
Presentation Outline

• Nitrogen Before Haber-Bosch Ammonia
• Fritz Haber, Carl Bosch, BASF and Anhydrous Ammonia
• Haber-Borsch Ammonia Production Starts
• Ammonia Production Expands
• Nitrogen Demand – Global and U.S. Profile
• Importance of Haber-Borsch N (nutrients) to mankind
1770’s - Birth of Modern Chemistry

Joseph Priestly
English Minister
(1733 - 1804)

Jan Ingenhousz
Dutch Physician
(1730 - 1799)

Discovered the Fundamentals of Photosynthesis

1770’s - Birth of Modern Chemistry

Carl Wilhelm Scheele
Swedish Chemist
(1742 – 1786)

Antoine Laurent Lavoisier
French Chemist
(1743 – 1794)

Daniel Rutherford
English Botanist
(1749 – 1819)
“discovered” N
to named “azote”


First Realization that Nitrogen Makes up Most of the Atmosphere

Source: Fertilizer Institute
1800’s - Value of N in Crop Production Demonstrated

Jean-Baptists Boussingault
French Chemist
(1802 – 1887)

Justin von Liebig
German Chemist
(1803 – 1873)

Scientific Experiments Left No Doubt About Nitrogen’s Crucial Role in Crop Production!

John Bennet Lawes
English Scientist
(1814 – 1900)

Joseph Henry Gilbert
English Chemist
(1817 – 1901)

Birth of Anhydrous Ammonia - NH₃

1784 – Berthollet becomes aware that the element “azote” joins with hydrogen to form ammonia

1795 – The first failed attempt to combine N and H

1800’s – Conducted experiments to synthesize ammonia

1900 – Ostwald though he had succeeded in synthesizing ammonia – Tests by Carl Bosch for BASF proved him wrong; NH₃ production was result of contaminants in machine

Nitrogen Sources: Pre Haber-Bosch

<table>
<thead>
<tr>
<th>Nitrogen Sources</th>
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<tr>
<td>Manures (barnyard and other)</td>
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<td>Guano (solidified bird excrement accumulated on subtrop/tropical islands)</td>
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<td>Chilean Nitrate (sodium nitrate)</td>
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<td>Coke-Oven Gas (by-product) Ammonium Sulfate</td>
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<td>- Coke oven gases produced primarily in the steel industry</td>
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<td>- Produced by reacting recovered coke oven ammonia with sulfuric acid</td>
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Nitrogen Fixation Processes:

- **Electric Arc Process (1901 – Niagara Falls)**
  
  Uses electrical current to combine N and oxygen in the air to form nitric oxide (NO)  
  \[ \text{(NO)} \rightarrow \text{Nitric Acid} \rightarrow \text{Calcium Nitrate/Sodium Nitrate} \]

- **Cyanamide Process (1907 – Italy)**
  
  Limestone burned to form calcium oxide; fused with coke in electric furnace  \[ \text{calcium carbide (CaC}_2\text{)} \] reacted with N at high temperature to form calcium cyanamide (CaCN$_2$)  
  \[ \text{Calcium cyanamide (CaCN}_2\text{)} \rightarrow \text{ammonia; ammonium phosphates; nitric acid; ammonium nitrate} \]

**Guano Extraction, Pre Haber-Bosch**

1840’s - Guano shipments to England and NY City - mostly from Peru

**1856 Guano Islands Act**
Congressional protection was afforded to discoverers of guano deposits off islands & reefs in the Caribbean and Pacific.

**Conversion rates:**
- 1860 & 1870: 12% N
- 1880: 7% N
- 1890: 4% N
- 1900: 3% N
- 1910 & 1913: 2% N

Chilean nitrates first reached the European and American markets in the 1840’s.

Coke-oven Gas (by-product) AS

Production, Pre Haber-Bosch

Pre Haber-Bosch N Production, Excluding Ammonia - 1913

Nitrogen Fixation Processes

Evaluating Haber’s Machine

Heinrich von Brunck
CEO of BASF

August Bernthsen
BASF Director of Research

Carl Bosch
BASF Chemist

Fritz Haber
Global N Production

1913 - 0.844 mil. tons N

Chilean nitrate (sodium nitrate)

Source: Morrison, 1937.
Global N Production

Source: Morrison, 1937.

1913 - 0.844 mil. tons N
1934 - 1.972 mil. tons N

Haber-Bosch 64%
By-product 18%
Cyanamide 11%
Chile 7%

Source: Morrison, 1937.
German Haber-Bosch Ammonia Production

Economic Recovery 1924-29

Economic Turmoil
Hitler Gains Power 1929-38

WW II 1939-45

Postwar Chaos

WW I 1914-18

U.S. Ammonia Production

1921: Atmospheric N Corp.
- Syracuse, NY
- Modified Haber-Bosch
- 15/40 tons per day
- Sold for refrigeration

1928: Allied Chemical
- Hopewell, VA
- 270 tons per day by 1930
- First to focus on fertilizer

WW I 1914-18

Great Depression 1929-41

Dust Bowl 1931-39

WW II 1939-45

U.S. Ammonia Production

U.S. emerges from WWII with strongest economy
Becomes largest global ammonia producer
Accounts for 1/3 of global production growth in 1950's
Set trends for modern day production:
- natural gas as hydrogen source
- plant location near feedstock and transportation
- integration of NH3 synthesis with downstream materials


Postwar Prosperity, 1945-1973

Growth in nutrient application rates, espec. corn & wheat

Adoption of hybrid corn varieties

Source: U.S. Geological Survey, IFA, TFI.
FSU Ammonia Production Surpasses U.S. in 1981

Source: U.S. Geological Survey, IFA, TFI.
1999-2008
High U.S. Natural Gas Prices
> 40% drop in Prod Capacity
CHINA

隨著食品在手，你安心

“With food in hand, you have peace of mind”
China - The Great Famine

Causes:
- Mao's Great Leap Forward => Including Ag. reforms
- Drought
- Floods
- Other

"Worst mass starvation in recorded history"

Estimated Deaths in Millions:
- 17 (Zhenghua - endorsed by Chinese Gov't)
- 30 (Bannister, 1987)
- 36 (Yang, 2008)
- 45 (Dikötter, 2010)
- 55 (Xiguang, 2005)

45 Million people is:
= 43 Largest U.S. Cities Today!
In 1958, only 12 countries with populations > 45 Mil., excl. China

Source: Tombstone, Yang Jinsheng, 2008; Mao's Great Famine, Frank Dikötter, 2010; U.S. Census Bureau.
China Ammonia Production, 1941-1960

1958 Population: 646.7 Million!

Great Famine

1960's - Minister of Chemical Industry:
- 10 ammonia plants, mostly medium sized
- 2 ammonia plants imported from:
  - Great Britain
  - Italy
- 1 urea plant imported from:
  - Netherlands

1973 - In response to rising demand, China imports 13 large ammonia-urea plants from:
- USA
- Netherlands
- Japan
- France


0.5 MMTN/year

Data Source: IFA.

1991: China Surpasses FSU as the Largest Ammonia Producer

FSU Production

Million metric tons N

Data Source: IFA.
Largest Ammonia Producing Countries

Data Source: IFA.

Production Increases by ~30 MMT NH₃!
Top 10 Ammonia Producing Countries in 2012

China NH3 Production
Nearly 4 times > Russian production
> next 6 largest producers combined

2nd-9th largest = 40% of global production

394 ammonia plants =>
53.6 MMT Material

Source: Data - IFA; No. of ammonia plants - Zhang and Huang, 2013 IFA PIT Conference, Oct 2013.
China - Urea Production

Largest Urea Importers - 1989-1992 Average

- China: 35.2%
- USA: 9.1%
- Vietnam: 4.5%
- Philippines: 2.8%
- India: 2.8%
- United Kingdom: 2.8%
- France: 2.6%

China Imports
6.9 MMT material

Data Source: IFA.
China - Urea Production

Largest Urea Exporters - 2012

- China: 16.2%
- Russia: 11.2%
- Qatar: 9.8%
- Ukraine: 8.4%
- Oman: 7.3%
- Saudi Arabia: 7.2%
- Iran: 6.7%

China Exports
6.9 MMT material

Data Source: IFA.

- 62 MMT Urea (material)
- 36 MMT Ammonia (2/3)
China: DAP Production

* 1997 - 40% of global DAP IMPORTS - 5.6 MMT material
* 2012 - 27% of global DAP EXPORTS - 10.7 MMT material
Net Difference - 16.3 MMT material

Data Source: IFA.
China: Phosphate Fertilizer Production

- 26.4 MMT Amm Phos Material
- 4.9 MMT Ammonia (9%)

Share of Global Production
1992 2012
- DAP 2% 42%
- MAP 0% 49%

Data Source: IFA.
Global Ammonia Production

> 99% of N production today is Haber-Bosch Synthesis!

Increased by 57 times since WWII

Global Nitrogen Use by Crop, 2010/11

- Wheat: 18%
- Corn: 17%
- Rice: 15%
- Vegetables: 9%
- Oilseeds: 7%
- Fruits: 6%
- Other Cereals: 5%
- Fiber Crops: 4%
- Sugar Crops: 4%
- Other: 15%

Source: IFA.
“Downstream” Nitrogen Fertilizers and Materials from Anhydrous Ammonia

100 years!

NH₃

Ammonia

Also used to produce plastics, synthetic fibers and resins, explosives, and numerous other chemical compounds.

About 87% for fertilizer!
World Nitrogen Fertilizer Use
2011 - 107.9 million metric tons N

- Urea 56%
- Ammonium Phosphates 7%
- Ammonium Nitrate 5%
- Nitrogen Solutions 5%
- Anhydrous Ammonia 4%
- Ammonium Sulfate 3%
- Other N 20%

Source: IFA.
World Nitrogen Fertilizer Use
2011 - 107.9 million metric tons N

China 31%
India 16%
USA 11%
Brazil 3%
Pakistan 3%
Indonesia 3%
Other 33%

Source: IFA.
China - Nitrogen Fertilizer Use
2011 - 33.8 million metric tons N

- Urea: 67%
- Ammonium Phosphates: 9%
- Other straight N: 17%
- Other N: 7%

Source: IFA.
India - Nitrogen Fertilizer Use
2011 - 17.4 million metric tons N

- Urea: 78%
- Ammonium Phosphates: 11%
- Other N: 11%

Source: IFA.
Global Nutrient Use, 1930-2011

- N use surpasses P₂O₅ use – 1960
- N use surpasses K₂O use – 1956
- USA: accounts for 35% of Global N Use – 1944
- China surpasses USA to become #1 in N Use – 1979
- India surpasses USA to become #2 in N Use – 1998
- Breakup of the FSU
- Recent growth

Source: Data from IFA.
Growth in Global Nitrogen Use
1999-2011: 23 MMTN

- China: 43% (9.9 MMT)
- India: 25% (5.8 MMT)
- Brazil: 8% (1.7 MMT)
- Other: 24%

>75%

Source: IFA.
U.S. Nitrogen Use by Crop, 2010/11

- Corn: 49%
- Wheat: 13%
- Fiber Crops: 5%
- Other Cereals: 3%
- Rice: 2%
- Oilseeds: 1%
- Vegetables: 1%
- Sugar Crops: 1%
- Fruits: 1%
- Other: 24%

Source: Computed from nutrient application rate data reported by USDA and Commercial Fertilizers, 2011.
Anhydrous Ammonia 27%
Nitrogen Solutions 27%
Urea 22%
Ammonium Phosphates 6%
Ammonium Sulfate 2%
Ammonium Nitrate 2%
Other N 14%

U.S. Nitrogen Fertilizer Use
FY2010/11 - 12.84 million tons N

Applying Anhydrous Ammonia

Side dressing nitrogen solutions

The Fertilizer Institute
U.S. Consumption of Selected Nitrogen Materials

- Nitrogen solutions
- Anhydrous ammonia
- Urea

Source: Commercial Fertilizers, 2011 and earlier issues.
U.S. Nitrogen Consumption: 1850 – 2010/11

13.2 Mil Short Tons N - FY2006/07

FY1953/54: N use surpassed K₂O use for good
FY1958/59: N use surpassed P₂O₅ use for 1st time

100 years to grow from 3 thousand to 1 Million Tons!

Source: Historical Statistics of the United States, U.S. Census Bureau; Commercial Fertilizers, various issues.
Media Focus

The Washington Post
Alarming ‘dead zone’ grows in the Chesapeake
By Darryl Fears. Published: July 24

A giant underwater “dead zone” in the Chesapeake Bay is growing at an alarming rate because of unusually high nutrient pollution levels this year, according to Virginia and Maryland officials. They said the expanding area of oxygen-starved water is on track to become the bay’s largest ever.

This year’s Chesapeake Bay dead zone covers a third of the bay, stretching from the Baltimore Harbor to the bay’s mid-channel region in the Potomac River, about 83 miles, when it was last measured in June. It has since expanded beyond the Potomac into Virginia, officials said.

Especially heavy fertilizer inputs into the bay by Maryland farmers, said Bruce Spaulding, an associate professor of environmental chemistry at the University of Maryland’s Center for Environmental Science.

Forbes
Scientists: Dead Zone Stressess Gulf, Action Needed

NEW ORLEANS — Scientists say the massive area of low oxygen in the Gulf of Mexico, known as the “dead zone” because it kills marine species, will create more problems unless fewer fertilizers are dumped into the Mississippi River.

The New York Times
Chemicals in Farm Runoff Rattle States on the Mississippi
By LESLIE KAUFMAN

As the surging waters of the Mississippi pass downriver, they leave behind flooded towns and inundated lives and carry forward a brew of farm chemicals and waste that this year — given record flooding — is expected to result in the largest dead zone ever in the Gulf of Mexico.

Dead zones have been occurring in the gulf since the 1970s, and studies show that the main culprits are nitrogen and phosphorus from excess fertilizer runoff. The river’s flow this year has been 40 percent greater than average.

Bradenton.com
Bill limiting local fertilizer regulation narrowly advances
By TONI WHITT - twhitt@bradenton.com

A controversial bill that would ban cities and counties from regulating fertilizer use and sales faced surprising resistance Wednesday from House Republicans. House Bill 457, designed to preempt local ordinances, passed the committee 8-7.

A similar Senate bill easily passed through committee unanimously.

Fertilizer Institute
Here’s My Plan to Improve Our World — And How You Can Help

Bill Gates, Wired.com, Nov. 12, 2013

“These days I get to spend a lot of time trying to advance innovation that improves people’s lives in the same way that fertilizer did.”
“… the lives of around half of humanity are made possible by Haber-Bosch nitrogen”

“The Haber-Bosch process has been of greater fundamental importance to the modern world than the airplane, nuclear energy, spaceflight or television”.


Thank You!