Nitrogen Fertilizer Production and Technology
The Nitrogen Cycle
Nitrogen Fertilizer Plays a Vital Role in Civilization

“Without the use of N fertilizers, we could not secure enough food for the prevailing diets of nearly 45% of the world’s population, or roughly 3 billion people…” [Smil, 2011]
Nitrogen-deficient plants are stunted, yellow, and poor yielding.
Twenty-two N-containing amino acids are naturally incorporated into polypeptides (protein).

Eight of these amino acids are essential for humans.
Organic Nitrogen Sources: Prior to Haber Bosch Process

Tankage: Animal by-products

Fishmeal: After oil extraction

Guano: Dried bird manure
Inorganic Nitrogen Sources: Prior to Haber Bosch Process

**Calcium Cyanamide**

\[ \text{CaC}_2 + \text{N}_2 \rightarrow \text{CaCN}_2 + \text{C} \]

**Chilean Nitrate:**
Mined from Atacama Desert

**Ammonium Sulfate:**
React coke by-product
\[ \text{NH}_3 \text{ with acid} \]
Food Crises Foreseen

“… all civilized nations stand in deadly peril of not having enough to eat.

… we are drawing on the earth’s capital, and our drafts will not be perpetually honoured.

The fixation of nitrogen is vital to the progress of civilized humanity.

Other discoveries will merely minister to our comfort, luxury, or convenience…”
1904... I supported the opinion that the technical realization of a gas reaction under high pressure was impossible.

1908... high temperatures (500-600 C), high pressures (100 atm) and osmium catalyst make the reaction possible.

\[ \text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3 \]
Nitrogen Fertilizer: A Simplified Process

Natural Gas → Carbon Dioxide

Air from atmosphere → Anhydrous Ammonia

Anhydrous Ammonia → Nitric Acid

Nitric Acid → Liquid Ammonium Nitrate

Liquid Ammonium Nitrate → Prill Tower or Granulator

Prill Tower or Granulator → Ammonia Nitrate

Ammonia Nitrate → UAN Solution

UAN Solution → Urea

Urea → Solid Urea

Solid Urea → Fertilizer, Feed, & Industrial

UAN Solution → Fertilizer

UAN Solution → Explosives & Fertilizer

Explosives & Fertilizer → Ammonia Nitrate

Ammonia Nitrate → Nitric Acid

Nitric Acid → Natural Gas

Fertilizer & Industrial

Ammonia

Nitric Acid

Industrial
Components of Ammonia Synthesis

Feedstock desulfurization:

The catalysts are very sensitive to S compounds present as impurities in natural gas and must be removed.

i. Hydro-desulfurization
   \[ R\text{-}SH + H_2 \rightarrow H_2S + RH \]

ii. Zinc adsorption
   \[ H_2S + ZnO \rightarrow ZnS + H_2O \]
Components of Ammonia Synthesis

Primary Reforming:

(reforming = producing H₂ gas)

1. Gas feedstock is heated to >500 C and enters nickel-based reforming catalyst.
   \[ CH_4 + H_2O \rightarrow CO + 3H_2 \]

   \[ CO + H_2O \rightarrow CO_2 + H_2 \]

(only 60% of CH₄ reacts in this step)
Components of Ammonia Synthesis

Secondary Reforming:

Unreacted/residual methane (~40%) is converted to hydrogen gas

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]
Components of Ammonia Synthesis

Shift Conversion:

Gases leaving secondary reformer contains 12 to 15% carbon monoxide

Another pass through a heated catalyst (Fe/Cr or Cu-based)

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
Carbon dioxide removal:

CO₂ is removed from the gas by absorption into alkanolamine or alkaline salt solutions

(Trace amounts of CO₂ and CO will later poison the ammonia synthesis catalyst)
Methanation:

Trace amounts of CO and CO₂ will poison the catalysts. They are converted back to methane.

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

Water also poisons the catalyst and must be removed.
Components of Ammonia Synthesis

Gas Compression:

Various compressors raise the pressure to between 80 to 300 bar.
Ammonia Synthesis:

High pressure (80 to 300 bar) Hot gas (350 to 550 C) is reacted with iron catalyst.

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]
Components of Ammonia Synthesis

Ammonia Refrigeration:

Gas is cooled to -33°C to liquefy ammonia, and pressurized for storage in insulated tanks.

Liquid ammonia is pumped to ships, barges, rail cars, or trucks for transportation.
Natural Gas is the Major Expense for Ammonia Synthesis

Natural Gas Price (US$/MMBTU)

IFA, 2011
World Ammonia Feedstock and Trends

IFA, 2011
### Various processes for synthesizing ammonia

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Relative energy consumption for making ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water electrolysis</td>
<td>$2H_2O \rightarrow 2H_2 + O_2$</td>
<td>300%</td>
</tr>
<tr>
<td>Coal gasification</td>
<td>$C + 2H_2O \rightarrow 2H_2 + CO_2$</td>
<td>170%</td>
</tr>
<tr>
<td>Naphtha reforming</td>
<td>$CH_2 + 2H_2O \rightarrow 3H_2 + CO_2$</td>
<td>104%</td>
</tr>
<tr>
<td>Natural gas reforming</td>
<td>$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$</td>
<td>100%</td>
</tr>
</tbody>
</table>

(Gosnell, 2005)
World Ammonia Production: Current & Forecast

5-year forecast
67 new plants (22 in China)
Top Ten Ammonia Producers (Capacity)

- Yara
- CF
- PCS
- Togliatti
- Agrium
- Sinopec
- IFFCO
- Koch
- EuroChem
- OCI
North America Ammonia Plants

A 3,000 mile ammonia pipeline
Ammonia Loading Facilities

Agrium; Kenai, Alaska (now closed)
International Ammonia Shipping
Barge Transport
Pressurized Railroad Cars

Anhydrous ammonia tank car with a capacity of 34,300 gallons
Ammonia Goes Into Many Products: Mostly N fertilizers
All commercial urea is produced through the reaction of ammonia and carbon dioxide:

\[
\begin{align*}
(1) & \quad 2\text{NH}_3 + \text{CO}_2 & \leftrightarrow & \text{NH}_2\text{COONH}_4 \quad \text{(at 200 C and 150 bar)} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{(ammonium carbamate)} \\
(2) & \quad \text{NH}_2\text{COONH}_4 & \leftrightarrow & \text{CO(NH}_2)_2 + \text{H}_2\text{O} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{(urea)} \\
& \quad \text{(urea solution then concentrated to “urea melt”)}
\end{align*}
\]

Urea melt dropped from prill tower or granulated in drum

\[2 \text{CO(NH}_2)_2 \text{ and excess heat } \rightarrow \text{Biuret and NH}_3\]
World Urea Production: Current & Forecast

- Asia: 2010: High, 2015e: Medium
- Mid East: 2010: Low, 2015e: Medium
- Africa: 2010: Medium, 2015e: Low
- FSU: 2010: Low, 2015e: Low (-3)
- North Amer: 2010: Low, 2015e: Low
- Latin Amer: 2010: Low, 2015e: Low
- Europe: 2010: Low, 2015e: Low (2)
- Oceania: Low

IFA, 2011, Fertecon
International Ammonia and Urea Trade
Ostwald Process: Making Nitric Acid

Ammonia is converted to nitric acid in a multi-step process:

1. Ammonia is oxidized in the presence of a catalyst (platinum/rhodium/900C)
   \[ 4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O} \]

2. Nitric oxide oxidized to nitrogen dioxide
   \[ 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \]

3. Nitrogen dioxide is readily absorbed by water, forming nitric acid
   \[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO} \]
Ammonia

Production: Reaction of hydrogen and nitrogen (Haber Bosch process)

Agronomic Use:
- Highest N content of any fertilizer
- When applied to soil, pressurized liquid immediately becomes vapor and reacts with water
- Aqua ammonia is made by dissolving ammonia in water (20 to 24% N solution)
- Ammonia must not be placed in close proximity to seeds
- Handling ammonia requires careful attention to safety

Non-Agricultural Use:
- Most ammonia is used as fertilizer, but it is important in many industrial applications
- It is an important refrigerant
- It has fuel potential too
Ammonia Refrigeration

Ammonia remains a popular refrigerant due to its favorable vaporization properties (evaporates at -32°C). It was commonly used before CFCs became widely available.

Ammonia is still widely used in industrial refrigeration applications because of its high energy efficiency and low cost.
Ammonia as a fuel

Ammonia Combustion

\[4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}\]

Heat of combustion comparison

<table>
<thead>
<tr>
<th>Fuel</th>
<th>BTU/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>20,400</td>
</tr>
<tr>
<td>Diesel</td>
<td>19,300</td>
</tr>
<tr>
<td>Ammonia</td>
<td>9,690</td>
</tr>
</tbody>
</table>
Urea:

**Production:** Reaction of ammonia and carbon dioxide

**Agronomic Use:**
- High solubility makes it useful for many purposes
- Rapid hydrolysis to ammonium can make it susceptible to volatile loss

**Non-Agricultural Use:**
- Used in many industrial chemicals
- Used in power plants and diesel exhaust systems to reduce emissions of nitrous oxide gases
- Common feed supplement for ruminant animals

**Formula:** CO(NH$_2$)$_2$

**N Content:** 46% N

**Solubility (20 C):** 1080 g/L
Selective Catalytic Reduction (SCR) controls nitrogen oxide emissions from stationary and mobile sources (reducing NO\textsubscript{x} to N\textsubscript{2} with a catalyst).

SCR cleans exhaustion gases when urea solution is injected as fine mist. Urea breaks down to ammonia, which is the NO\textsubscript{x} reducing agent.

\[ 4\text{NO} + 2(\text{NH}_2)\text{CO} + \text{O}_2 \rightarrow 4\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2 \]

Urea consumption for trucks is about 3% of diesel use.

An average large truck will need to refill a 20-gal tank of 32% urea solution about every 5,000 miles.
Ammonium Nitrate

Formula: NH$_4$NO$_3$
N Content: 33 to 34% N
Solubility (20 C): 1900 g/L

Production: Reaction of ammonia and nitric acid

Agronomic Use:
- High solubility makes it useful for many purposes
- Often used when nitrate source of nutrition is desired
- Low ammonia volatility makes it desirable for surface fertilizer applications

Non-Agricultural Use:
- Low-density prilled ammonium nitrate is used widely as explosive in the mining industry
- Low-density (porous) material allows rapid absorption of fuel oil
- Instant cold packs are made with ammonium nitrate. Highly endothermic reaction rapidly occurs when water is added (cools to 2 to 3C).
Ammonium Sulfate

Formula: \((\text{NH}_4)_2\text{SO}_4\)
N Content: 21% N
Solubility (20 \(\text{C}\)): 750 g/L

**Production:** Reaction of heated ammonia and sulfuric acid

**Agronomic Use:**
- Commonly used where both N and S are required by plants
- Useful where nitrate is not desired
- Used in post-emergence herbicide sprays

**Non-Agricultural Use:**
- Used in bread products as a dough conditioner
- Used in fire extinguisher powder/flame-proofing agents
- Common in chemical, wood pulp, textile, and pharmaceutical industries
Urea Ammonium Nitrate (UAN)

Production: Reaction of heated solutions of urea and ammonium nitrate

Agronomic Use:
- High solubility makes it useful for many purposes
- Half of the N comes from urea and half from ammonium nitrate
- UAN is compatible with many chemicals, often added to irrigation water, or used as a foliar nutrient source

Formula: CO\((\text{NH}_2\)_2 + \text{NH}_4\text{NO}_3\)
N Content: 32% N (or less)
(N content depends on cold temp)
**Ammoniated Phosphate**

**Monoammonium Phosphate**
- Formula: $\text{NH}_4\text{H}_2\text{PO}_4$
- Nutrient Content: 10 to 12% N, 48 to 61% $\text{P}_2\text{O}_5$
- Solubility (20 C): 370 g/L
- Solution pH: 4 to 4.5

**Diammonium Phosphate**
- Formula: $(\text{NH}_4)_2\text{HPO}_4$
- Nutrient Content: 18% N, 46% $\text{P}_2\text{O}_5$
- Solubility (20 C): 580 g/L
- Solution pH: 7.5 to 8

**Production**: Reaction of ammonia and phosphoric acid

**Agronomic Use**:
- Primarily used as a source of highly soluble phosphorus
- Useful where additional N is desired

**Non-Agricultural Use**:
- Used in various food products
- Used in fire extinguisher powder/flame-proofing agents
- Feed ingredient for animals
Potassium Nitrate

Formula: KNO₃
N Content: 13% N
Solubility (20 C): 316 g/L

Production: Reaction of potassium chloride with a nitrate source

Agronomic Use:
- High solubility makes it useful for many purposes
- Often used where chloride is undesirable
- Valuable source of potassium

Non-Agricultural Use:
- Has long been used for fireworks and gunpowder
- Used in food to maintain quality of meat and cheese
- Added to specialty toothpastes
- Used for storing heat in solar energy installations
Additional information on plant nutrient production and management are available from the IPNI website:

www.ipni.net