AMMONIA OVERVIEW
Background and History
Economics
Plant Information

WHY DO WE NEED SYNTHETIC NITROGEN FERTILIZER?
• Nitrogen is a vital nutrient for plants
• Population growth hurt food supply
• Natural fertilizer reserves were depleted
• Nitrogen in the atmosphere is in stable, unreactive form

EARLY AMMONIA HISTORY
• 1909 – Fritz Haber fixed nitrogen in air in a lab experiment
• 1913 – Carl Bosch, BASF, developed industrial scale process
  • Water Gas Shift
  • Iron Ammonia Catalyst
• 1921 – Casale designed their first ammonia converter
• 1928 – Uhde’s first ammonia plant 100 t/d
• 1943 – Kellogg licenses its first ammonia plant
• 1960s – Haldor Topsoe pioneers radial flow converters
• 1963 – Kellogg pioneers first centrifugal compressors
• 1966 – CF Braun first Purifier™ NH3 plant on line
• 1970s – Kellogg standardizes the 1000 t/d plant
• 1971 – Kellogg’s first horizontal converter
AMMONIA CONVERTER (OPPAU/LUDWIGSHAFEN—1913)

RECENT HISTORY
• 1980s – Kellogg develops low-energy design
• 1990s – Casale axial radial converter design
• 1990s – Merger of Braun Purifier & Kellogg conventional design
• 1990s – Prereformer Revamps
• 2000s – HTI, KBR, & Uhde develop large capacity designs
• 2010s – Gas Heated Reformer Revamps

AMMONIA END USES
• Fertilizer - 80%
• Metals processing, explosives, plastics, cleaning agents and other industries.
• Industrial Refrigeration

AMMONIA PRODUCTION BY GLOBAL REGION

WHERE AMMONIA IS PRODUCED AND CONSUMED

AERIAL VIEW OF LIMA, OH
• Plant is located in populated area and close to city
PLANT INFORMATION

- Number of employees varies, between 100-250
  - Operations
  - Maintenance
  - Engineering
- Footprint
  - Ammonia & Urea: 1000’x700’
  - Offsites

ROUGH PRODUCTION ECONOMICS

- Main production cost is the feedstock, which is natural gas.
- Ammonia production responsible for ~17% of the energy used in the chemical/petrochemical sector
- About 27-32 MMBtu of natural gas is required to produce 1 ton of ammonia.
- Right now Ammonia is selling for about $710 per ton in the midwest, and $450 per ton on the Gulf Coast.
- At $710/ton price and $4/MMBtu gas, profit is ~$500/ton.

AMMONIA PRODUCTION COST

- Feedstock
  - Natural gas and coal are the primary feedstocks for ammonia production
  - Natural gas cost is 75% of ammonia production cost excluding capital cost
  - Coal cost is 62% of ammonia production cost excluding capital cost
- Capital Cost
  - Natural gas based plant capital cost is 47% of ammonia production cost
  - Coal gasification based plant capital cost is 66% of ammonia production cost

AMMONIA COST VS NATURAL GAS COST

- The price of natural gas is a key metric in the nitrogen business: a $1 per MMBtu increase adds around $33 to the cost of manufacturing one short ton of ammonia.

AMMONIA AND UREA PRODUCTION COSTS BY GLOBAL REGION

- Ukraine and Western Europe set floor price for ammonia and urea.

AMMONIA DEMAND AND CAPACITY OVER TIME

- China accounts for the largest share of projected new capacity.
- The world wide demand for nitrogen products is driven by increased demand for nitrogen based fertilizers.
- Estimated capacity to be added over the next few years is illustrated in this graph.
Nitrogen presents good opportunity to upgrade natural gas.

Ammonia Trade Global Profile

China has periodically been the world's largest urea exporter, although its annual volume fluctuates with changes in government export policies. United States urea imports averaged 27,000 short tons in 2011.

Fertilizer World Outlook 2014-2018
International Fertilizer Industry Association (IFA)

- Nearly 200 fertilizer projects planned, $110 B in investments
- Projected 146 mtpy (30%) increase in global fertilizer product capacity
- Ammonia
  - Projected 30% increase in industrial nitrogen demand
  - 15.5% supply increase from 153 mtpy to 176 mtpy
  - 9.1% demand increase from 148 mtpy to 161 mtpy
- Urea
  - 60 new urea plants projected (25 in China)
  - 14.8% supply increase from 188 mtpy to 216 mtpy
  - 12.6% demand increase from 180 mtpy to 203 mtpy

Nitrogen Fertilizer Prices Since 2000

Changes in fertilizer price generally reflect those seen for ammonia.

Projected Natural Gas Prices

Henry Hub Natural Gas Price

Source: EIA, Energy Information Administration, August 2014

Notes: Cost of natural gas to power plants is shown for some years, but does not include all of the natural gas being consumed.
PROCESS OVERVIEW

AMMONIA PRODUCTION

AMMONIA PLANT

STEAM REFORMING CHEMISTRY

Reforming Converts hydrocarbons (C_xH_y) to Syngas (H_2+CO)

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &\rightarrow \text{CO} + 3\text{H}_2 & \text{highly endothermic} \\
\text{C}_x\text{H}_{(2x+2)} + n\text{H}_2\text{O} &\rightarrow n\text{CO} + (2n+1)\text{H}_2 & \text{highly endothermic}
\end{align*}
\]

Shift converts CO to H_2 (no catalyst needed above 1500 F)

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} &\rightarrow \text{CO}_2 + \text{H}_2 & \text{mildly exothermic}
\end{align*}
\]

Requires heat input

- Desulfurized feed + MP steam preheated to 900-1200 F
- Hot combustion gas provides heat into catalyst tubes in primary reformer
- Steam to Dry Gas Ratio typically 3.0 to 3.2 prevents C laydown

STEAM REFORMING CHEMISTRY

- Steam methane reforming equilibrium favored by:
  - Lower pressure
  - Higher temperature
  - High steam to carbon ratio
- CO shift to H_2 equilibrium favored by:
  - Lower temperature
  - High steam to carbon ratio
- Steam methane reforming reactions are slower than CO shift
- Steam methane reforming and CO shift reactions are reversible
SECONDARY REFORMER

Oxidation
Oxidation provides heat for reforming
Oxidation adds nitrogen in stoichiometric ratio needed for NH₃

\[ xCH₄ + yCO + zO₂ \rightarrow (x+y)CO₂ + 2xH₂O \text{ exothermic} \]

Water Gas Shift
Shift converts CO to H₂

\[ CO + H₂O \rightarrow CO₂ + H₂ \text{ exothermic (going to CO₂)} \]

REFORMING

REFORMING

REFORMING
**SHIFT REACTION**

Water Gas Shift
Shift converts CO to H₂

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \text{ exothermic (going to CO}_2) \\
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \text{ exothermic (going to CO}_2)
\]

\[K = \frac{p(\text{CO}_2) \cdot p(\text{H}_2)}{p(\text{CO}) \cdot p(\text{H}_2\text{O})}\]

Where: \(p()\) is the partial pressure of the gas in atmospheres (abs).

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**SHIFTS**

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**CO₂ REMOVAL**

- After shifting of CO to CO₂ (previous step) to purify the syn gas.
- Any oxide poisons synthesis catalyst (CO, CO₂, water, oxygen)
- High percentage removal desired to minimize methanation losses (next step)
- If making Urea, CO₂ needed as a feed stream

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**METHODS OF CO₂ REMOVAL**

- Solid bed quick cycle mol sieve units
  - Won’t produce pure CO₂ stream for urea
- Scrubbing Processes:
  1. Physical solvents
  2. Chemical solvents

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**PHYSICAL SOLVENTS**

- Uses gas solubility properties under pressure for absorption and reduction in pressure to release dissolved gases
- Takes fairly high pressure for absorption
- Requires large circulation volumes
- Adequate for bulk removal only – won’t produce a high purity syn gas
- Examples are water, Fluor Solvent, Selexol, Rectisol

**CHEMICAL SOLVENTS**

- Strong alkaline solvents like MEA don’t really require high gas treating pressures:
  - High regeneration heat requirement
  - Moderate circulation rates
- Somewhat weaker alkaline solvents like activated potassium carbonate, and activated MDEA require higher gas treating pressures:
  - Low regeneration heat requirements
  - Somewhat higher circulation rates

**BENFIELD**

**METHANATION**

- Required to remove residual CO and CO2 from syn gas
- CO poisons ammonia synthesis catalyst
- CO reacts with NH3 to form solid carbamate
  \[ \text{NH}_2\text{CO}_2\text{NH}_4 \]
- The easiest and most economical method to remove residual CO and CO2 is to react with hydrogen to make methane
  \[
  \begin{align*}
  \text{CO} + 3\text{H}_2 &\rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{exothermic} \\
  \text{CO}_2 + 4\text{H}_2 &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \text{exothermic}
  \end{align*}
  \]

**SYNGAS COMPRESSION**
**SYN GAS COMPRESSOR**

**AMMONIA SYNTHESIS**

Haber Bosch Ammonia Synthesis

\[ \text{N}_2 + 3\text{H}_2 \rightarrow (\text{injected magnetite}) \quad 2\text{NH}_3 \quad \text{exothermic} \]

- Clariant (Sud Chemie) AmoMax wustite based catalyst developed in China starting in 1986. First commercial charge installed in 2003. Produces more ammonia than magnetite.

**AMMONIA IS HARD TO MAKE**

Thermodynamic equilibrium of synthesis reaction

\[ 1.5 \text{H}_2 + 0.5 \text{N}_2 = \text{NH}_3 \]

limits conversion of \( \text{H}_2 \) and \( \text{N}_2 \) to \( \text{NH}_3 \)

Ammonia synthesis equilibrium is favored by low temperature and high pressure

**RELATIVE SYNTHESIS REACTION RATE**

‘CD’ is maximum reaction rate curve

\[ 1.5 \text{H}_2 + 0.5 \text{N}_2 = \text{NH}_3 \]

**1,000 TPD KELLOGG CONVERTER**

Original Axial Flow 4-Bed Quench

Retrofit Radial-Flow Topsoe S-200
QUENCH CONVERTER TEMPERATURE PROFILE

Bed sequence follows maximum rate curve

RADIAL FLOW WITH INTERBED HEAT EXCHANGE—TEMPERATURE PROFILE

Heat exchange causes no dilution from quenching

CASALE ISOTHERMAL CONVERTER

Radial-flow converters were a major improvement in plant performance

BENEFITS OF HIGHER CONVERSION

• Less recycle gas flow
  • Lower syn gas compressor horsepower
• Higher ammonia dewpoint in converter effluent
  • Refrigeration duty shifts to higher temperatures
  • Lower refrigeration compressor horsepower
• Better plant efficiency
• Debottlenecks syn loop in existing plants
  • Higher ammonia production

AMMONIA CONVERTERS
Low ammonia concentration (<25 mole%) in reactor outlet means lots of unreacted gas.
Recycle unreacted gas from reactor back to reactor in “loop”, after separating product ammonia.
Recycle concentrates inerts (methane, argon) in reactor.
Must purge some unreacted gas from synthesis loop to limit buildup of inerts.
Maintain circulating gas at 3:1 H:N ratio for highest conversion to ammonia.

Inerts methane and argon don’t participate in synthesis, take up space.
Syngas is purged from loop to limit buildup of inerts.
- Purged syn gas is a loss of unconverted H₂ and N₂.
- Need more makeup gas to replace purged gas to maintain production rate.
There is a balance between benefit of lowering loop inerts versus cost of lost H₂ and N₂ in purge gas.
Typical converter inlet is 8-15 mole% methane + argon.
AMMONIA SYN LOOP

HYDROGEN RECOVERY

- Processes to recover H2 from high-pressure syn loop purge gas
  - Membrane separation
  - Cryogenic separation
- Relatively pure H2 is recovered and returned to loop makeup gas
- N2, CH4, Ar are rejected and sent to primary reformer fuel
- Less process feed natural gas is needed with purge gas recovery

Watch out for helium when present, it is concentrated in loop by purge gas recovery

HIGHER VALUE PRODUCTS

Urea
Diesel Exhaust Fluid
Ammonium Nitrate
Urea-Ammonium Nitrate
Ammonium Thiosulfate
Ammonium Polyphosphate

AMMONIA PRODUCTS

AMMONIA USES AND TOP WORLD PRODUCERS
**UREA USES**
- Fertilizer (~90%)
  - Granules
  - Urea-ammonium-nitrate aqueous solution
- Plywood
  - Urea-formaldehyde
  - Urea-melamine-formaldehyde
- Selective Catalytic Reduction (SCR) of NOx Emissions
  - Power generation flue gas
  - Diesel engine exhaust gas
- Explosives
  - Urea-nitrate

**UREA SYNTHESIS**
- Urea is made from ammonia and carbon dioxide at high pressure (2000 psig) and high temperature (350 to 400 F).
- Urea is formed in a two-step reaction
  \[ 2 \text{NH}_3 + \text{CO}_2 \leftrightarrow \text{NH}_2\text{COONH}_4 \text{ (ammonium carbamate)} \]
  \[ \text{NH}_2\text{COONH}_4 \leftrightarrow \text{H}_2\text{O} + \text{NH}_2\text{CONH}_2 \text{ (urea)} \]
- Urea synthesis is exothermic. The urea synthesis reactor is cooled by generating low pressure steam in coils inside the reactor.
- Raw urea from the reactor contains unreacted NH3 and CO2 and ammonium carbamate. As the pressure is reduced and heat applied the NH2COONH4 decomposes to NH3 and CO2. The ammonia and carbon dioxide are recycled.

**UREA SYNTHESIS WITH CO2 STRIPPING**

**UREA DEMAND FOR DIESEL EXHAUST FLUID**
- Urea-based SCR is being integrated into global vehicle platforms.

**UREA AMMONIUM NITRATE (UAN)**
- UAN is a commonly used fertilizer in the US Midwest for corn.

| Physical and Chemical Characteristics of UAN Solutions |
|-----------------|-----------------|-----------------|
| Grade, %N:       | 28              | 30              | 32              |
| Ammonium nitrate, %: | 40              | 42              | 45              |
| Urea, %:         | 30              | 33              | 35              |
| Water, %:        | 30              | 25              | 20              |
| Specific gravity at 16 °C: | 1.283           | 1.303           | 1.320           |
| Salt-out temperature (°C): | -18             | -10             | -2              |

**COKE GASIFICATION TO UAN PLANT**
ADDITIONAL HIGHER VALUE PRODUCTS

- Ammonium Thiosulfate
  - Excellent source of sulfur for plant nutrition
  - 12% N, 26% S
- Ammonium Polyphosphate
  - 10% N, 34% Phosphate

EMISSIONS AND WASTEWATER

- Ammonia Process Emissions
- Urea Process Emissions
- Water Supply
- Waste Water

AMMONIA PLANT EMISSIONS

- Typical Combustion Products
  - Nitrogen Oxides (NOx)
  - Carbon Monoxide (CO)
  - Carbon Dioxide (CO₂)
  - Methane (CH₄)
  - Nitrous Oxide (N₂O)
  - Volatile Organic Compounds (VOCs)
- Sulfur Dioxide and Particulate Matter (Trace Amounts)

PRIMARY REFORMER EMISSIONS

- Process condensate contains the following:
  - Nonmethane Organic Compounds
  - Carbon Dioxide
  - Ammonia
- Medium pressure steam used to strip process condensate

CO₂ REMOVAL

- CO₂ must be removed from process gas
- Emissions
  - Carbon Monoxide
  - MEA/Piperazine (activator)
  - VOCs
  - Ammonia

CO₂ is often used onsite to make urea.

CONDENSATE STRIPPING

- Process condensate contains the following:
  - Nonmethane Organic Compounds
  - Carbon Dioxide
  - Ammonia
- Medium pressure steam used to strip process condensate
OTHER PRODUCT EMISSIONS

- Urea
  - Ammonia
  - Particulate matter
- Ammonium Nitrate
  - Ammonia
  - Nitric acid
  - Particulate matter
- Nitric Acid
  - Nitric oxide
  - Nitrogen dioxide

WATER OVERVIEW

- The purpose of water/wastewater treatment is:
  - To provide for efficient, cost effective production
  - To protect/preserve capital investment
  - To make efficient use of water resources
  - To meet regulatory requirements

AMMONIA PLANT WATER MASS BALANCE

MAKEUP WATER

- River Water
- City Water
- Well Water

PRETREATMENT

- Water pretreatment is the process of preparing the plant raw water supply for direct use or further treatment
- Consequently, the level of pretreatment varies according to the raw water supply and plant usage
  
PRETREATMENT

- Softening
  - Precipitation process used to reduce scaling constituents primarily due to hardness
  - Softening also reduces silica levels
  - Softening is induced principally by the addition of lime and soda ash
**Filtration**
- Removal of suspended solids by flow through filtration media
- Generally used as a polishing step following pretreatment or a stand-alone process
- Filter media material and grade can be specified to accomplish specific tasks

**Pretreatment**

**HIGH PURITY TREATMENT**
- Reverse Osmosis
- Ion Exchange

**COOLING TOWER CHEMISTRY**

<table>
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<th>Analysis</th>
<th>Frequency</th>
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<td>Specific Conductance</td>
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<td>Shift</td>
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<tr>
<td>Silica</td>
<td>Shift</td>
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<tr>
<td>Chloride</td>
<td>Shift</td>
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<tr>
<td>Total Alkalinity</td>
<td>Shift</td>
</tr>
<tr>
<td>Iron</td>
<td>Shift</td>
</tr>
<tr>
<td>Free Chlorine</td>
<td>10 minutes following chlorination</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>10 minutes following chlorination</td>
</tr>
</tbody>
</table>

**Boiler Chemistry**
- **Boiler Feedwater**
  - Total Hardness: Non-Detect
  - Dissolved O₂: 0.007 mg/l
- **Boiler Water**
  - Specific Conductivity: ≤ 150 μS/cm
  - Silica: ≤ 2 mg/l

Limits from ASME Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers for 1,500 psi Drum Operating Pressure.
WASTEWATER TREATMENT
- Priority Pollutants
- pH
- Suspended Solids
- Chlorine
- Nutrients
- Temperature
- Total Dissolved Solids

WASTE WATER
- Collection ponds used to collect wastewater and separate oils
  - Cooling Tower Blowdown
  - Process Sewers

WASTEWATER TREATMENT
- Recycle supply
  - Plant drains
  - Filter backwash
  - Boiler blowdown
  - RO reject water
  - Storage area runoff
  - Cooling Towers
- Recycle users
  - Cooling Towers
  - Boiler Makeup

SITE AERIAL VIEW

STORAGE AND TRANSPORTATION
Storage Systems
Storage Capacity
Transportation Methods

NH3 STORAGE
NH3 Storage and Handling regulated by:
- 29 CFR 1910.111- Storage and Handling of Anhydrous Ammonia
- ANSI K61.1- Safety Requirements for the Storage and Handling of Anhydrous Ammonia
PROCESS FLOW DIAGRAM

PROCESS FLOW DIAGRAM KEY COMPONENTS
- Cold Ammonia Storage Tanks
- Transfer Pumps
- Ammonia Shell and Tube Heaters
- Warm Ammonia Storage Bullets
- Warm Ammonia Transfer Pumps
- Trucks / Railcars

COLD AMMONIA STORAGE TANKS
- Pressurized vessels practical to ~ 300 tons NH3
- Fully Refrigerated or Semi-Refrigerated
- 126 to 170 ft diameter
- 60 to 105 ft high
- 15-30,000 tons capacity (6 to 12 million gallons)

STORAGE TANK CONSTRUCTION TYPES
- Single Containment
- Double Containment
- Full Containment

REFRIGERATED TANKS
- Heat leaks in from environment
- Refrigeration required for atmospheric storage
- Components include compressor, intercooler, condenser, and receiver

AMMONIA TRANSPORT BY TRUCK
AMMONIA TRUCK TRANSPORT SAFEGUARDS

- Two sets of internal closing valves
  - Emergency shut-off
- Minimum two safety relief valves

AMMONIA TRANSPORT BY RAIL

EXISTING AMMONIA RAIL CAR FLEET

- Number of Cars in Service: ~ 6,000
- Average Age of Fleet (est.): 25 years
- Maximum Allowable Service Life: 40 years

AMMONIA PIPELINES

- Magellan Ammonia Pipeline
  - 1,100 miles
  - 20 terminals Texas to Minnesota
  - Delivery Capacity: 900,000 tons/yr
  - 528,000 tons Storage
- Kaneb Pipeline
  - 2,000 miles
  - 24 terminals, Louisiana to Nebraska & Indiana
  - Delivery Capacity: 2 million tons/yr
  - 1 million tons Storage

REFRIGERATED BARGES

- Existing Ammonia Barge Fleet
  - 2,500 ton Capacity
  - Age of current fleet: ~ 40 years
  - 31 Barges in Service
  - Mississippi River System
  - Inter-Coastal Waterway
  - Pacific Northwest

US AMMONIA INFRASTRUCTURE

- Ammonia Plants
- Storage Tanks
- Import Terminals
- Kaneb Pipeline
- Magellan Pipeline
SAFETY

Ammonia Properties
Exposure
Response
Leaks
Fire

SAFETY CLASSIFICATIONS

• DOT: Hazardous Material
• OSHA: Hazardous Material
• EPA: Extremely Hazardous Substance

AMMONIA PROPERTIES AND LEAK RESPONSE CONSIDERATIONS

• Colorless liquid, pungent odor
• Boiling Point -28°F
• Vapor at atmospheric conditions
• Liquid under pressure
• Water soluble

AMMONIA EXPOSURE

Ammonia vapors are hazardous, causing respiratory distress and injury.

OSHA RESPONSE LEVELS

• First Responder
  - Initial response
  - Defensive response
  - Containment

• Hazardous Materials Technician
  - More aggressive, offensive role
  - Purpose of stopping release

RELEASE PHASES

Release phases depend on wind/weather conditions and amount of release.
ENVIRONMENTAL IMPACTS OF RELEASE

- Run off
- Keep out of drains and waterways
- Water can be used to spray on vapors, but must be trapped.

A little NH3 will drastically affect water pH

AMMONIA FIRE HAZARDS

- NH3: Small Flammability Range, 15-28%
- Syngas is highly flammable because of its H2 content

FIRE PROTECTION AND SAFEGUARDS

- NFPA 72 Standards
- Fire Monitoring and Alarms
  - UV/IR Flame Detectors
  - Smoke Alarms
  - LEL Gas Detectors
- Fire Suppression
  - Protect Equipment
  - Contain Fire

AMMONIA FIRE RESPONSE

- MSDS Recommendations
  - Extinguish with water or dry chemical spray
  - NFPA Fire Rating
    - Flammability: 1
    - Health Hazard: 3
    - Reactivity: 0

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