Efficient Ammonia Production

Jim Gosnell
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Hydrogen Conference
Argonne National Laboratory
Topics to be Covered

• Overview of KBR Activities
• Ammonia Supply & Demand
• History of Ammonia Manufacture
• Ammonia Plant Market Trends
• Current Manufacturing Technology
• Ammonia from Renewable Energy
• Summary
Organization (Cont’d)

KBR

Energy & Chemicals Division

- Process Technology
  - Development
  - Licensing
- Engineering
- Procurement
- Construction
- Operations
- Maintenance

Government & Infrastructure Division

Largest government logistics & services contractor with premier worldwide civil infrastructure capabilities

- CFO
- Legal
- Administration
KBR E&C Business Lines

Gas Monetization

Oil & Gas

Refining

Petrochemicals

Syngas
Overview of Syngas Markets

- Ammonia
- Hydrogen
- Methanol
- GTL
- Urea
- Other Fertilizers
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• Summary
## Demand for Basic Chemicals-2004

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Millions MT/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid</td>
<td>167</td>
</tr>
<tr>
<td>Ammonia</td>
<td>142</td>
</tr>
<tr>
<td>Urea</td>
<td>121</td>
</tr>
<tr>
<td>Ethylene</td>
<td>105</td>
</tr>
<tr>
<td>Chlorine</td>
<td>50</td>
</tr>
<tr>
<td>Soda</td>
<td>43</td>
</tr>
<tr>
<td>Methanol</td>
<td>35</td>
</tr>
</tbody>
</table>

Sources: Purvin & Gurtz, SFA Pacific, Fertecon.
Ammonia Uses

Fertilizers
82%

Other Uses
18%
- explosives
- fibers
- resins
- animal feed
World Arable Land

Millions of hectares

Source: SRI

- Rest of World
- Southwest Asia
- Socialist Asia
- FSU
- Europe
- North America

KBR
Energy and Chemicals
World Population

Average Annual Growth Rate = 1.35%

Source: EIA
World Ammonia Capacity
(Source – Fertecon)

Average annual growth:
2000-2010 = 1.6%/year
2005-2010 = 2.2%/year

For 2005-2010 this equates to
5 to 6 new plants/year @ 2000 mt/d
World Ammonia Capacity & Demand
(Source-Fertecon)

**Installed Capacity**
- 125
- 135
- 145
- 155
- 165
- 175
- 185
- 195

**Demand**

![Graph showing World Ammonia Capacity & Demand from 2000 to 2010. The graph displays the increase in capacity and demand over the years, with capacity rising steadily and demand showing a similar upward trend.]
Implications of Capacity/Demand Curves

• Required plant availabilities to satisfy anticipated demand are in the range of 80 to 85%

• Industry is capable of plant availabilities in the range of 91-92%

• This means ~40,000 mt/day of capacity is idle. Much of this idle capacity is in:
  – United States
  – Eastern Europe

• Outlook is for continued rationalization of high cost producers & shift to low gas-cost regions
Trends in World Ammonia Exports
(Percent of World Production)

75% of new capacity in next few years is aimed at the export market.
Net World Ammonia Trade in MM MT/Year
(Plus=export, minus=import)

Total trade in 2004 = 17.9 mt   (Fertecon)
Net trade in 2004 = 9.9 mt (Estimate)
Historical US Gulf Coast NH₃ Prices
(Fertecon, current dollars)

US$/tonne fob, Quarterly range

- Oil price shock due to Yom Kippur War/OPEC embargoes
- New capacity in Trinidad & Qatar, increased production in Algeria
- Extreme volatility in US gas prices
- PCS closes Trinidad capacity due to lack of gas price agreement
- FSU gas prices in $ terms collapse with Rouble devaluation
- 1 mill t increase in US imports in 1994/ increase in Ukrainian gas costs
- Fertrin plants o/s in Trinidad 1981/2
- Fall in European fertilizer demand / new units in Belgium and Turkey displacing imports
- Oil prices fall
- Bahrain plant o/s 1985
- New Saudi plant o/s 1987
- India cuts NH₃ imports
- Extreme volatility in US gas prices

70 71 72 73 74 75 76 77 78 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 0 1 2 3 4
Predicted US Gulf Coast NH₃ Prices
(Fertecon, current dollars)

Current $/tonne

Price cfr Tampa/USG
Supply Cost fob USG plant

Forecasts assume base case US gas prices
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History of Ammonia Manufacture

- Ammonia is synthesized from hydrogen and nitrogen

\[ 3H_2 + N_2 \rightleftharpoons 2NH_3 \]

- Nitrogen source is always air

- Hydrogen source has varied over the years
Discovery of Hydrogen

• Described by Robert Boyle in 1671
  \[ \text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2 \]

• Recognized as an element in 1766 by Henry Cavendish

• Named by Antoine Lavoisier in 1783 after he discovered its ability to generate water
  \[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]
History of Hydrogen Production

- First commercial production in early 19th century making town gas from coal
  \[ \text{Coal} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + \text{CH}_4 \]

- In early 20th century, coke and coal were gasified with either air or oxygen to produce \( \text{H}_2 \) + CO mixtures for chemical synthesis

- First steam-methane reformer on-line in 1931
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \]
# Hydrogen Sources for Making Ammonia

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Approximate Relative Energy Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water electrolysis</td>
<td>$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$</td>
<td>300%</td>
</tr>
<tr>
<td>Coal gasification</td>
<td>$\text{C} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{CO}_2$</td>
<td>170%</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>$\text{CH} + 2\text{H}_2\text{O} \rightarrow 2\frac{1}{2} \text{H}_2 + \text{CO}_2$</td>
<td>135%</td>
</tr>
<tr>
<td>Naphtha reforming</td>
<td>$\text{CH}_2 + 2\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$</td>
<td>104%</td>
</tr>
<tr>
<td>Nat. gas reforming</td>
<td>$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2$</td>
<td>100%</td>
</tr>
</tbody>
</table>
# History of Ammonia Manufacture

<table>
<thead>
<tr>
<th>Event</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia consists of hydrogen &amp; nitrogen</td>
<td>1784</td>
</tr>
<tr>
<td>First equilibrium test by Haber</td>
<td>1904</td>
</tr>
<tr>
<td>Haber patent</td>
<td>1908</td>
</tr>
<tr>
<td>Catalyst program by Haber &amp; BASF</td>
<td>1908 - 1922</td>
</tr>
<tr>
<td>Equipment program begun by Bosch at BASF</td>
<td>1910</td>
</tr>
<tr>
<td>First commercial plant - 30 mt/d at BASF</td>
<td>1914</td>
</tr>
<tr>
<td>World capacity reaches 2000 mt/d</td>
<td>1927</td>
</tr>
<tr>
<td>World capacity reaches 450,000 mt/d</td>
<td>2005</td>
</tr>
</tbody>
</table>
Topics to be Covered

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Market Situation – Old Plants

• Older plants often struggle to remain competitive
  – Old technology which is less efficient
  – Located in high gas cost area
  – Smaller capacities

• Energy efficiency revamps have already taken place

• Many operators debottleneck existing capacity to improve economy of scale
New Plant Trends in Energy Consumption

- Theoretical Minimum

Gcal/mt - LHV

- 1940
- 1950
- 1960
- 1970
- 1980
- 1990
- 2000
Ammonia Plant New Capacity by Region

Projects shift to ME and LA where gas is available at lower cost and to APAC (higher consumption growth)

Source: KBR
Average Capacity Built by Decade
KBR Licensed Plants

Metric Tons/Day

<table>
<thead>
<tr>
<th>Decade</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950s</td>
<td>0</td>
</tr>
<tr>
<td>1960s</td>
<td>500</td>
</tr>
<tr>
<td>1970s</td>
<td>1000</td>
</tr>
<tr>
<td>1980s</td>
<td>1500</td>
</tr>
<tr>
<td>1990s</td>
<td>2000</td>
</tr>
<tr>
<td>2000s</td>
<td>2500</td>
</tr>
</tbody>
</table>
History of Maximum Size NH₃ Plants

Year

MT/D


2X

2X

2X?
Indicative Capital Cost
(Assumes 0.7 exponent)
Trends in Maximum Capacity

• All licensors are now claiming that they can design single-train plants for >3000 mt/day

• KBR has a 2200 mt/day plant under construction in Australia

• KBR is willing to offer and guarantee a single-train 4000 mt/day plant

• KBR internal studies have shown that a single train capacity of 5000 mt/day is possible
Market Implications – Capacity Trend

• There will be fewer projects

• Large amounts of ammonia (& urea) will suddenly come on the market

• Projects will require more capital, leading to increased industry partnering to share risks

• These “mega-capacity” projects will be in low gas cost areas
Market Implications (Continued)

• These “mega-capacity” plants will be located at coastal sites

• There will be some logistics issues moving large volumes of product

• Plants that are older, smaller, and in locations with high feed costs will continue to shut down
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Sections in an Ammonia Plant

- **Feed Treatment**
- **Syngas Production**
- **Syngas Purification**
- **Synthesis Loop**

- **Natural Gas Feed**
- **Process Air**
- **Steam & Water System**
- **Carbon Dioxide**
- **Ammonia**
- **Make-up Water**
- **Condensate**
### Chemistry of Syngas Production

<table>
<thead>
<tr>
<th>Process</th>
<th>Chemical Reaction</th>
<th>Favorable Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Reforming</td>
<td>heat + CH(_4) + H(_2)O → 3H(_2) + CO</td>
<td>High temp &amp; High stm/carbon</td>
</tr>
<tr>
<td>Secondary Reforming</td>
<td>O(_2) + 2H(_2) → 2H(_2)O + heat</td>
<td>High temp &amp; High stm/carbon</td>
</tr>
<tr>
<td></td>
<td>heat + CH(_4) + H(_2)O → 3H(_2) + CO</td>
<td></td>
</tr>
<tr>
<td>High temp shift</td>
<td>CO + H(_2)O → CO(_2) + H(_2) + heat</td>
<td>Low temperature High steam/CO</td>
</tr>
<tr>
<td>Low temp shift</td>
<td>CO + H(_2)O → CO(_2) + H(_2) + heat</td>
<td>Low temperature High steam/CO</td>
</tr>
</tbody>
</table>
## Engineering of Syngas Production

<table>
<thead>
<tr>
<th>Process</th>
<th>Equipment</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Reforming</td>
<td>Catalyst-packed tubes in a furnace</td>
<td>Nickel catalyst</td>
</tr>
<tr>
<td>Secondary Reforming</td>
<td>Refractory-lined pressure vessel</td>
<td>Nickel catalyst</td>
</tr>
<tr>
<td>High temp shift</td>
<td>Pressure vessel</td>
<td>Iron-chrome catalyst</td>
</tr>
<tr>
<td>Low temp shift</td>
<td>Pressure vessel</td>
<td>Copper-zinc catalyst</td>
</tr>
</tbody>
</table>
Primary Reforming

Fuel

Air to Secondary Reformer

To Feed Treatment

Reformer Outlet 700 °C

Mixed Feed

Feed

Air

Steam

BFW

ID Fan

Superheated Steam
Secondary Reforming

Excess Air

Primary Reformer Effluent

700 °C

100-125 bar Steam

To High Temperature Shift Reactor

870 °C

BFW
Shift Conversion

Syngas from Boiler

High Temperature Shift Reactor

BFW Heating & Steam Generation

Low Temperature Shift Reactor

Water Cooler

Process Cond.

Separator

Shifted Syngas to CO₂ Removal

Cond.

Water Cooler

BFW Heating & Steam Generation

370 C

430 C

200 C

240 C

35 C
## Chemistry of Syngas Purification

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Favorable Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Removal</td>
<td>Physical Dissolution or Chemical Reaction</td>
<td>Low temp &amp; High pressure</td>
</tr>
</tbody>
</table>
| Methanation            | \[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\] | 280 - 350°C          |
<p>| Drying                 | Physical Adsorption to remove water &amp; CO₂        | 2 - 4 °C             |
| Cryogenic Purification | Separation of argon, residual CH₄ and excess N₂ from syngas | -180 °C             |</p>
<table>
<thead>
<tr>
<th>Process</th>
<th>Equipment</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Removal</td>
<td>Absorb/regen columns with solution circulation pumps</td>
<td>Contact syngas with solution over packing</td>
</tr>
<tr>
<td>Methanation</td>
<td>Pressure vessel</td>
<td>Nickel catalyst</td>
</tr>
<tr>
<td>Drying</td>
<td>Two pressure vessels each with a filter</td>
<td>Cyclic operation of mol sieve desiccant</td>
</tr>
<tr>
<td>Cryogenic Purification</td>
<td>Plate fin exchanger, expander, column</td>
<td>Aluminum, generator brake, trays, set H/N = 3.0</td>
</tr>
</tbody>
</table>
Syngas Purification

- Raw Syngas from Shift
- CO₂ Regenerator
- CO₂ Absorber
- Methanator
- Dryers
- Cryogenic Purifier
- Waste Gas to Fuel
- Pure, Dry Syngas to Compressor
- Process Condensate to Stripper
- Synloop Purge
KBR Cryogenic Purifier

Waste Gas to Fuel

Syngas from Dryers

Vol%:
- H₂: 62-68
- N₂: 30-35
- CH₄: 2-3
- A: ~0.6

H₂/N₂ = 3
Inert <0.3%

Syngas to Compresso

-182°C
CO$_2$ Removal System
1500 t/d plant in China
KBR Cryogenic Purifier
1850 t/d plant in Holland
<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Favorable Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis</td>
<td>$3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3 + \text{heat}$</td>
<td>Low T &amp; high P</td>
</tr>
<tr>
<td>Heat Recovery</td>
<td>Generate 100 bar+ steam</td>
<td>High T</td>
</tr>
<tr>
<td>Product Recovery</td>
<td>Condense via refrigeration</td>
<td>Low T &amp; High P</td>
</tr>
</tbody>
</table>
# Engineering of Ammonia Synthesis

<table>
<thead>
<tr>
<th>Process</th>
<th>Equipment</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis</td>
<td>Catalyst filled pressure vessel</td>
<td>P = 90 – 175 bar</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T = 400 - 500 C</td>
</tr>
<tr>
<td>Heat Recovery</td>
<td>Shell &amp; tube heat exchanger</td>
<td>Proprietary design</td>
</tr>
<tr>
<td>Product Recovery</td>
<td>Compression refrigeration system</td>
<td>Ammonia as the refrigerant</td>
</tr>
</tbody>
</table>
Refrigeration System

- Ammonia Accumulator
- Condenser
- Refrigeration Compressor
- HP Case
- LP Case
- Unitized Chiller
- Warm NH₃
- Cold NH₃
- -33 C
- 0 bar-g

NH₃ from Letdown Drum
Single-case Synthesis Gas Compressor
Ammonia Converter
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Ammonia from Water Electrolysis
Conceptual Process Scheme

Air

Air Sep Unit

O₂ & A

Circulation & Refrigeration Compressors

Ammonia Synthesis Loop

Ammonia

Air Compressor

N₂

Elect. Cells

H₂

100 bar-g

O₂

Water
<table>
<thead>
<tr>
<th>Component</th>
<th>IN</th>
<th>OUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td>1.67</td>
</tr>
<tr>
<td>Argon</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>2.68</strong></td>
<td><strong>2.68</strong></td>
</tr>
</tbody>
</table>

Material Balance
(tons/ton of ammonia – assumes no losses)
# Electric Power Input to Process

<table>
<thead>
<tr>
<th></th>
<th>kWh/MT of NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressors</td>
<td>390</td>
</tr>
<tr>
<td>Pump</td>
<td>8</td>
</tr>
<tr>
<td>Electrolytic cells</td>
<td>7000 – 9000</td>
</tr>
<tr>
<td>TOTAL</td>
<td>~7400 – 9400</td>
</tr>
</tbody>
</table>

(1) Based on 3.5 – 4.5 kWh/Nm³ of H₂
## Approx. Energy Consumption of Process

<table>
<thead>
<tr>
<th></th>
<th>GCal/MT of NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity @ 860 kcal/kWh</td>
<td>6.4 – 8.1$^{(1)}$</td>
</tr>
<tr>
<td>Heat recovery from loop</td>
<td>-0.6</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>5.8 – 7.5</td>
</tr>
</tbody>
</table>

$^{(1)}$ Based on 3.5 – 4.5 kWh/Nm$^3$ of H$_2$
## Approx. Energy Consumption (Cont’d)

<table>
<thead>
<tr>
<th></th>
<th>Gcal/Metric Ton NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>860 kcal/kWh</td>
</tr>
<tr>
<td>Electricity (1)</td>
<td>6.4</td>
</tr>
<tr>
<td>Heat recovery</td>
<td>-0.6</td>
</tr>
<tr>
<td>TOTAL</td>
<td>5.8</td>
</tr>
</tbody>
</table>

(1) Based on 3.5 kWh/Nm³ of H₂

(2) Conversion of primary energy to electricity at 40% efficiency.
**Approx. Variable Operating Cost**

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity @ $0.035/kWh</td>
<td>259</td>
</tr>
<tr>
<td>Water @ $5/1000 gallons</td>
<td>2</td>
</tr>
<tr>
<td>By-product O₂ @ $25/t</td>
<td>-42</td>
</tr>
<tr>
<td>Heat recovery @ $40/Gcal</td>
<td>-24</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$195</strong></td>
</tr>
</tbody>
</table>

(1) Based on 3.5 kWh/Nm³ of H₂
NH$_3$ as Auto Fuel – Supply & Demand

- Daily WORLD ammonia capacity
  - Is about 450,000 tons
  - Corresponds to about $8 \times 10^6$ million Btu

- Daily US demand for gasoline
  - Is about $9 \times 10^6$ barrels$^{(1)}$
  - Corresponds to about $47 \times 10^6$ million Btu

(1) US DOE, EIA
Ammonia as Auto Fuel

• Fuel Price Comparison
  – $\text{NH}_3 \text{ @ }$400/mt = $23/mm Btu
  – Gasoline @ $3/gal = $24/mm Btu

• Ammonia Storage Issues
  – Boiling point @ 14.7 psia is minus 28 F
  – Storage requires either
    • Refrigeration at atmospheric pressure
    • Pressurization to ~ 20 atmospheres
Implications for NH$_3$ as Auto Fuel

- US gasoline demand is about six times the world’s installed ammonia capacity

- Ammonia via electrolysis with power @ $0.035$/kWh may be competitive at today’s ammonia prices

- To satisfy 10% of US gasoline market with NH$_3$ via electrolysis requires ~ 80,000 to 100,000 MW, depending on assumed efficiency of electrolytic cells

- Installed US electric power plant capacity (2000) is about:
  - 605,000 MW for utility owned
  - 210,000 MW for non-utility owned

- There will be some ammonia storage issues
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Ammonia Technology Summary

1970s – a decade of rapid capacity expansion

1980s – a decade of reduced energy consumption
Ammonia Market Summary

1990s – a decade of moving projects to low gas cost areas

2000s – a decade of increased plant capacities
Ammonia Market Summary (Cont’d)

• A lot of capacity will come on line in next four years

• This will drive ammonia prices down towards their historic average of about $150/mt

• Which will cause further capacity rationalization in high gas cost areas
Ammonia via Electrolysis

- Technically feasible but current technology\(^{(1)}\) limits:
  - Cells at 100 bar to \(~3600\) kg/year of hydrogen
  - Cells at 1 bar to \(~380,000\) kg/year of hydrogen

- Capital cost issues
  - Capital cost of scheme has not been estimated
  - Do electrolytic cells have economy of scale?

- Operating cost issues
  - Requires very cheap power to be competitive
  - Reliability of cells may be an issue

\(^{(1)}\) NREL Report, Sept 2004
Ammonia as Auto Fuel - Issues

• To meet 10% of US gasoline demand from NH₃ via electrolysis will consume about:
  – 80,000-100,000 MW of electric power @ 3.5 kWh/Nm³ of H₂
  – Ammonia equivalent to 60% of world capacity

• Ammonia is classified as a toxic chemical

• Ammonia Handling
  – Distribution
  – Storage
  – Transfer to vehicle tank