Syngas to Ammonia
The Industrial Gas Route to a Faster Project Cycle at Reduced Cost

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Praxair at a Glance

- A Fortune 300 company with 2015 sales of $11 billion
- Doing business in more than 50 countries
- 26,000 employees
- One million customers worldwide
Praxair Global Hydrogen - USGC Operations

- +1 bscfd H2 production capacity on USGC
- 220 MMscfd new H2 capacity under construction
- 310 miles of H2 pipelines linking key petrochemical hubs
- 46 mile H2 pipeline (& N2) to Freeport just commissioned
- 2.5 bscf H2 cavern storage located mid-system to add responsiveness and reliability
Ammonia

- Ammonia
  - >146 MM metric tons production in 2015¹

- One of the most important basic chemicals
  - primarily used in agricultural (~75% of production)
  - a key raw material for industrial chemicals (e.g. acrylonitrile, nitric acid, caprolactam)

- Produced for over 100 years via the Haber-Bosch process
  - \(3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3\)
  - beloved of chemistry teachers the world over as a way of introducing Le Chatelier’s principle

- \(\text{H}_2\) typically produced from steam reforming of natural gas or gasification of coal/petcoke

- \(\text{N}_2\) introduced in an air-blown ‘secondary’ reforming step or via air-separation
Ammonia Production - Conventional

- **Desulphurization** in a two step process:
  - Sulfur compounds catalytically hydrogenated to $\text{H}_2\text{S}$:
    - $\text{H}_2 + \text{RSH} \rightarrow \text{RH} + \text{H}_2\text{S}$
  - Hydrogen sulfide removed by zinc oxide:
    - $\text{H}_2\text{S} + \text{ZnO} \rightarrow \text{ZnS} + \text{H}_2\text{O}$
- **Reforming** in a two step process to achieve correct H/N ratio:
  - Primary reforming:
    - $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ (reforming)
    - $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ (shift)
  - ‘Air-blown’ secondary reforming (additional reactions):
    - $\text{CH}_4 + 2\text{O}_2 + 8 \text{N}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 8\text{N}_2$
    - $\text{CH}_4 + 3/2 \text{O}_2 + 6 \text{N}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO} + 6\text{N}_2$
- **Catalytic shift conversion** to convert CO to $\text{CO}_2$ and $\text{H}_2$:
  - $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
- **Carbon dioxide removal** via an amine process
- **Methanation** to remove residual amounts of CO or $\text{CO}_2$:
  - $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$
  - $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
- **Compression**
- **Ammonia conversion**
  - $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$

Source: European Fertilizer Manufacturers’ Association®
Ammonia Production - Conventional
Ammonia Production - Conventional

- Most process steps are associated with feedstock conditioning and/or production of syngas
- Ammonia production step itself straightforward
- Elimination of front-end processing could significantly reduce complexity and costs
- . . . How can you eliminate these steps?
Ammonia Production – High Purity H2 & N2

- Compression
- Ammonia conversion
  - $3H_2 + N_2 \rightarrow 2NH_3$

- Desulphurization in a two step process:
  - Sulfur compounds catalytically hydrogenated to $H_2S$:
    - $H_2 + RSH \rightarrow RH + H_2S$
  - Hydrogen sulfide removed by zinc oxide:
    - $H_2S + ZnO \rightarrow ZnS + H_2O$

- Reforming in a two step process to achieve correct H/N ratio:
  - Primary reforming:
    - $CH_4 + H_2O \rightarrow CO + 3H_2$ (reforming)
    - $CO + H_2O \rightarrow CO_2 + H_2$ (shift)
  - 'Air-blown' secondary reforming (additional reactions):
    - $CH_4 + 2O_2 + 8N_2 \rightarrow 2H_2O + CO_2 + 8N_2$
    - $CH_4 + 3/2O_2 + 6N_2 \rightarrow 2H_2O + CO + 6N_2$

- Catalytic shift conversion to convert CO to CO$_2$ and $H_2$
  - $CO + H_2O \rightarrow CO_2 + H_2$

- Carbon dioxide removal via an amine process

- Methanation to remove residual amounts of CO or CO$_2$
  - $CO + 3H_2 \rightarrow CH_2 + H_2O$
  - $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

- Compression

- Ammonia conversion
  - $3H_2 + N_2 \rightarrow 2NH_3$
Ammonia Production - High Purity H2 & N2
High Purity vs. Conventional

- **Significant scope reduction**
  - Lower Capex – by as much as 50%
  - Less complex and faster construction cycle
  - Lower plant maintenance costs

- **Lower Emissions**
  - No fired heaters – and no NOx, SOx, VOC’s, CO, CO₂
  - No CO₂ emissions from reforming
  - Faster permitting

- **Higher efficiency/conversion**
  - Minimal inerts (CH₄, Ar) → reduced purge
  - Higher capacity for same ‘loop’ → built-in expansion capability

- **Less steam integration complexity**
  - Insufficient steam to meet all power needs without ‘front-end’
    - export steam and run all electric (syngas compressor, makeup compressor)
  - Import/produce additional on-purpose steam
H2 Production

- H2 predominantly produced by steam methane reforming
- H2 is also a by-product of other industrial chemical processes
  - ethylene cracking
  - propane dehydrogenation (PDH)
  - chloralkali production
  - CO production (for acetic acid, isocyanates, etc.)
- Globally competitive natural gas pricing in the US has been a catalyst for unprecedented chemical growth
  - Approximately 15 MM metric tons per year of new ethylene capacity and 3 MM metric tons per year of new PDH capacity have been announced/underway
  - > 750 MMscfd H2 by-product . . . in theory
- The drawback of by-product H2 is that it is a by-product . . .
  - reliability of supply is a key concern
- How can you take advantage of these new sources without sacrificing reliability?
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H2 Cavern Storage

- Cavern storage effectively converts by-product H2 to firm supply . . . critical if H2 is a key feedstock
- Commercial operation since 2007
- Salt caverns widely used for hydrocarbon storage
  - . . . first time for high purity H2
- Praxair proprietary and patented technology²,³,⁴
Yara-BASF Freeport Project

- Yara and BASF announced in 2015 the development of a world-scale 750 kta ammonia facility in Freeport, Texas\(^6,8\)
- Based on “hydrogen and nitrogen” technology
- $600MM investment between Yara and BASF
  - Yara focus on merchant market
  - BASF focus on downstream derivatives (caprolactam, isocyanates)
- KBR providing EPC and licensing ammonia synthesis technology\(^9\)
- Praxair providing the H2 and N2 to the venture as part of a nearly $400MM project to extend supply systems to Freeport, Texas\(^10\)
  - 170 MMscfd H2 and 2000 tpd N2 under 20 year agreement
  - 46 mile pipeline extensions from Texas City to Freeport
  - Adding new capacity to the system
- On track to start-up in 2017
PSA H2 Recovery and Pipeline Projects
Conclusion

- Using high purity H2 and N2 can facilitate the development of a world-scale ammonia project that:
  - Requires lower CAPEX than a conventional ammonia project
  - Is faster to develop and at lower risk
  - Has a higher capacity/efficiency
  - Has lower emissions and is faster to permit
  - . . . and is globally competitive

- The key is to secure access to reliable and competitive supplies of H2 and N2
References
