Efficient Ammonia Production

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13 October 2005

Hydrogen Conference

Argonne National Laboratory

KBR

Energy and Chemicals

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

Halliburton Company

- *Energy Services Group*
  - Landmark
  - HALLIBURTON (Energy Services)
- *Engineering & Construction*
  - KBR

Organization (Cont'd)

KBR

Energy & Chemicals Division

Process Technology
Development
Licensing
Engineering
Procurement
Construction
Operations
Maintenance

Government & Infrastructure Division

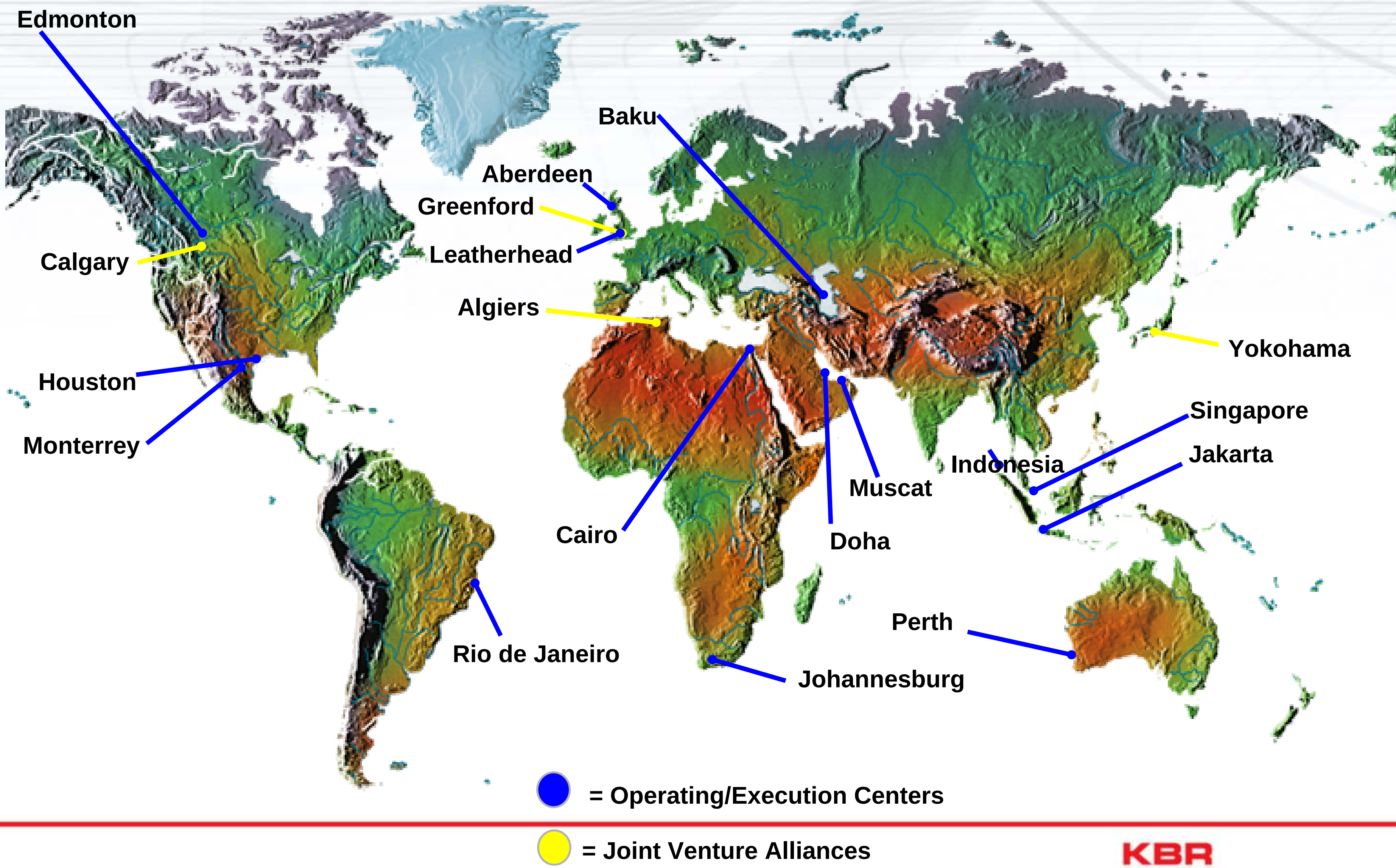
Largest government logistics & services contractor with premier worldwide civil infrastructure capabilities

CFO

Legal

Administration

KBR Energy & Chemicals Operations



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KBR E&C Business Lines

Gas Monetization

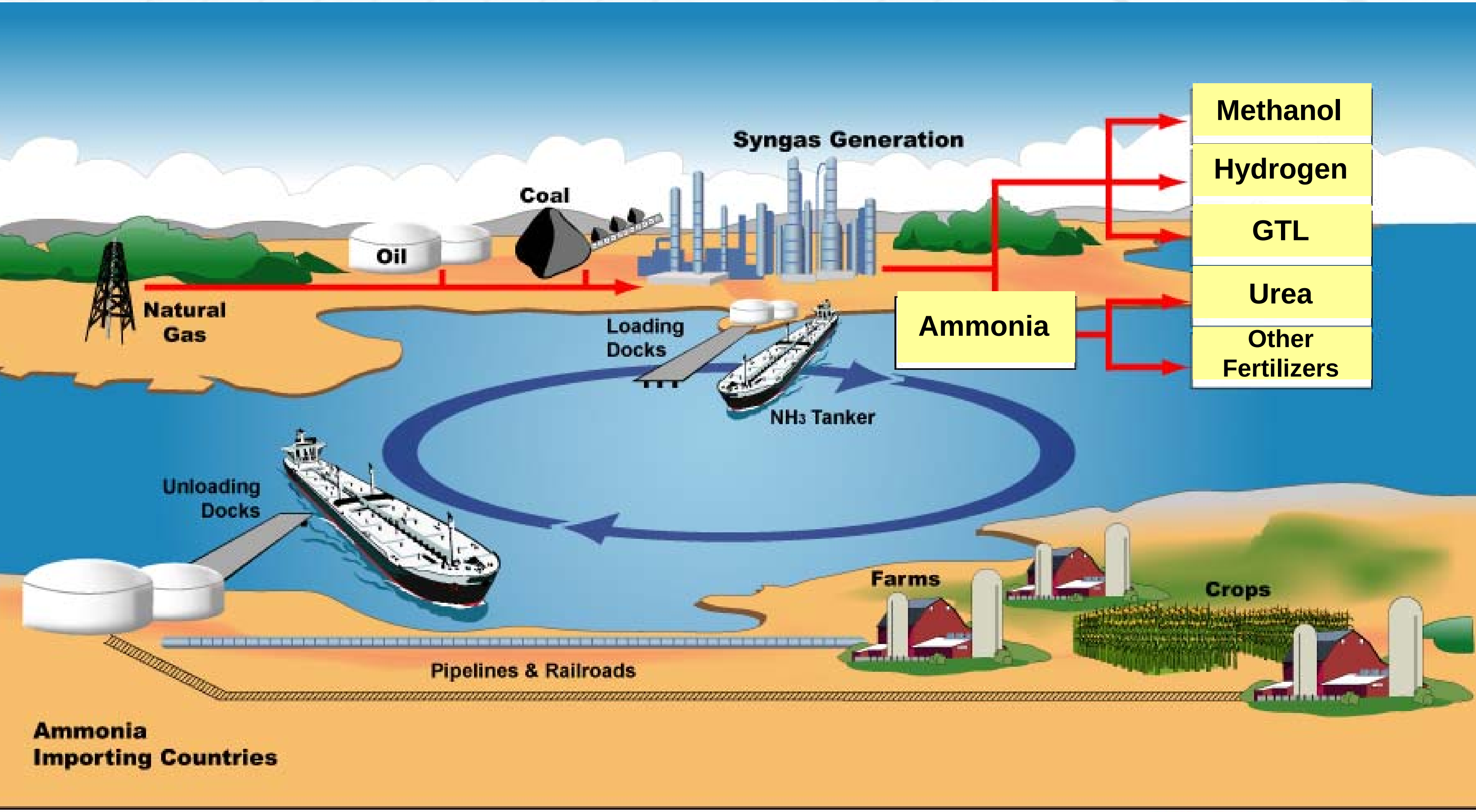
Oil & Gas

Refining

Petrochemicals

Syngas

Overview of Syngas Markets



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Demand for Basic Chemicals-2004

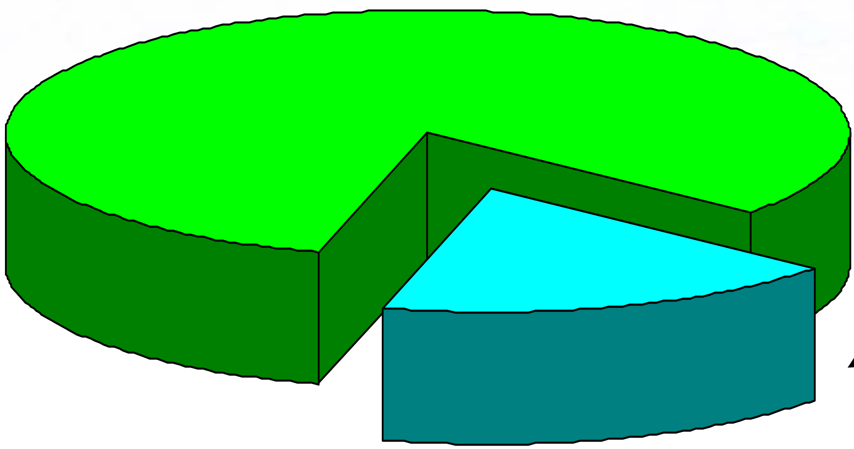
	Millions MT/Year
Sulfuric acid	167
Ammonia	142
Urea	121
Ethylene	105
Chlorine	50
Soda	43
Methanol	35

Sources: Purvin & Gurtz, SFA Pacific, Fertecon.

Ammonia Uses

Fertilizers

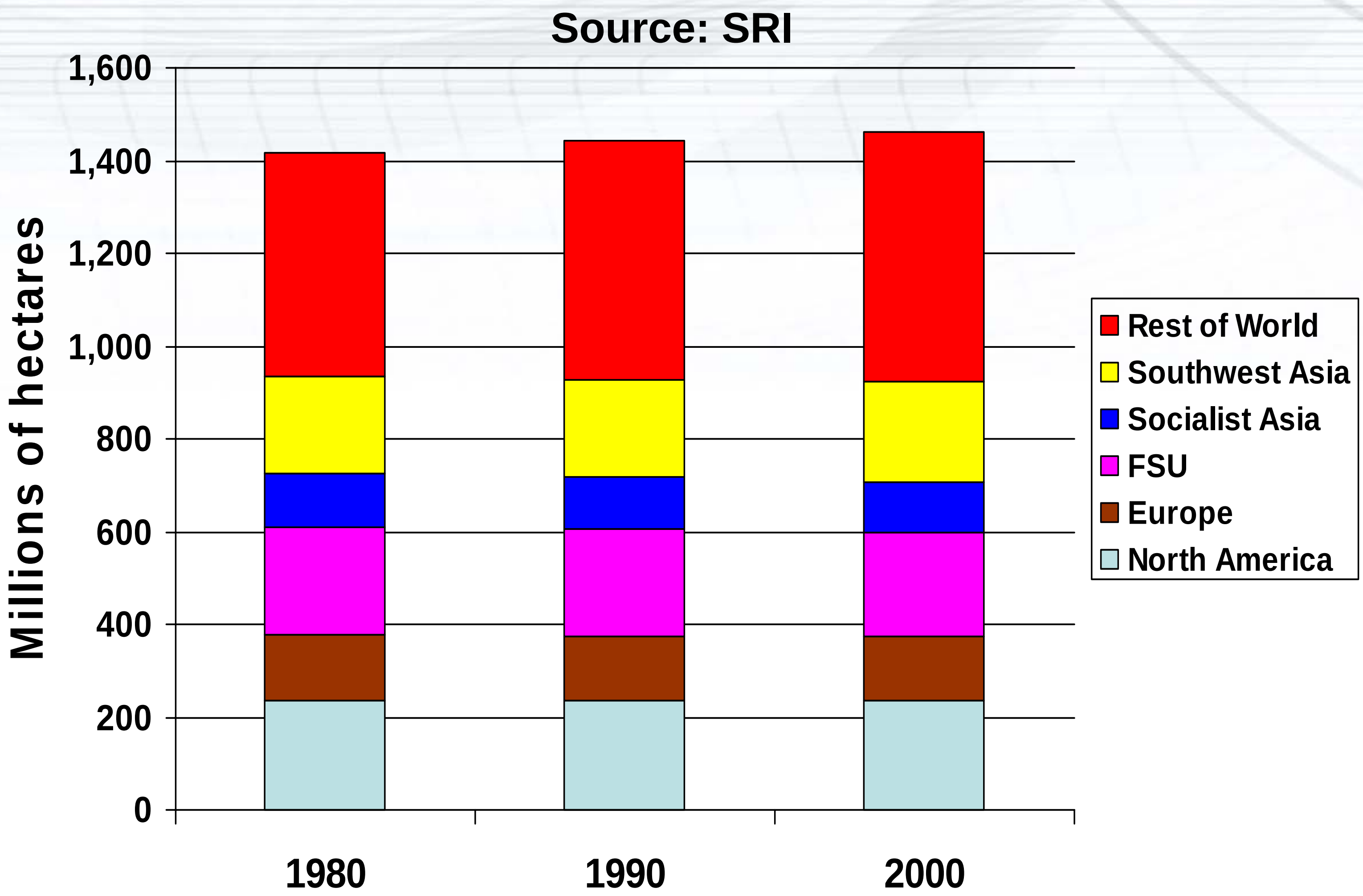
82%



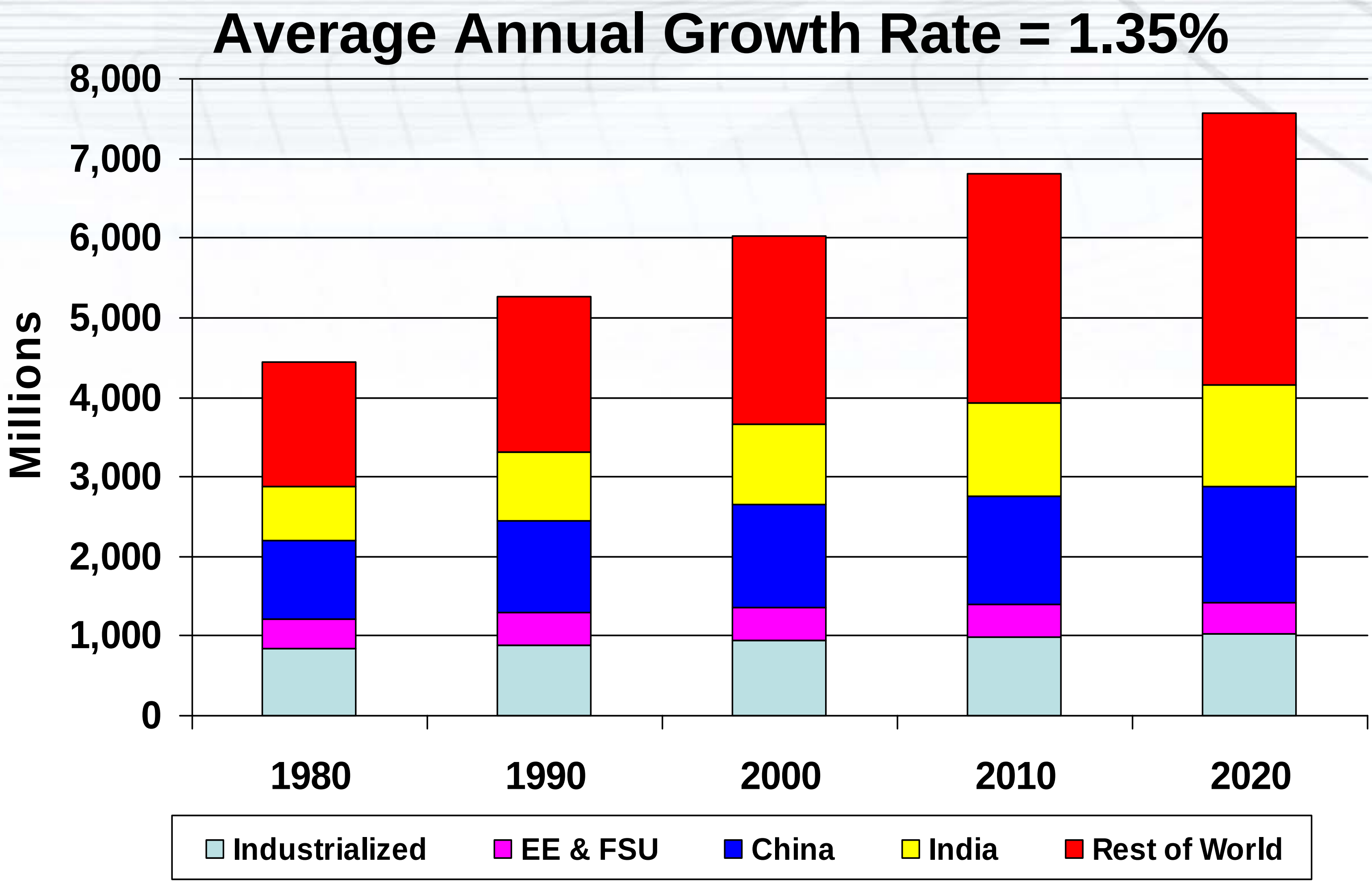
Other Uses
18%

- explosives
- fibers
- resins
- animal feed

World Arable Land



World Population



Source: EIA

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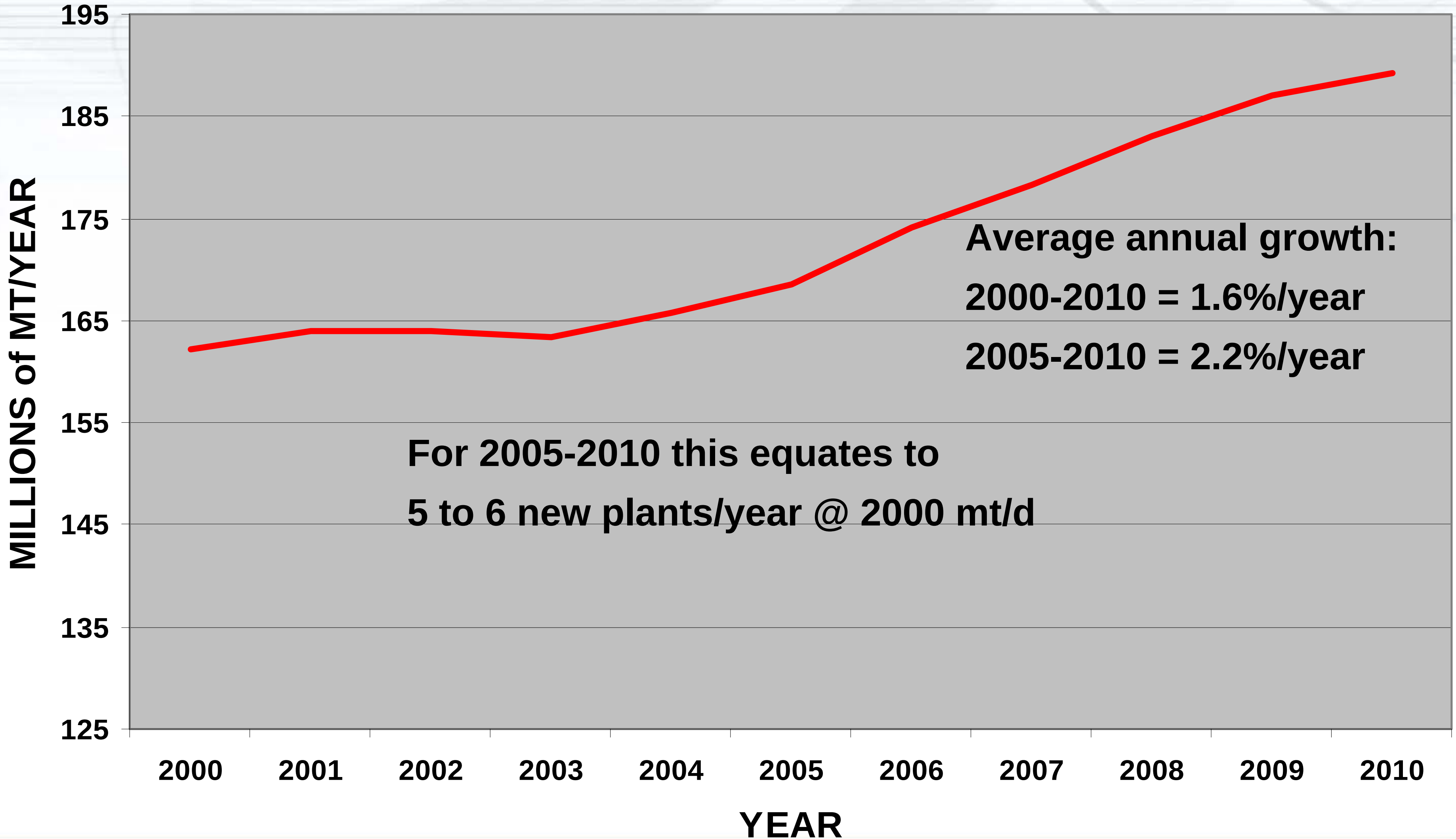
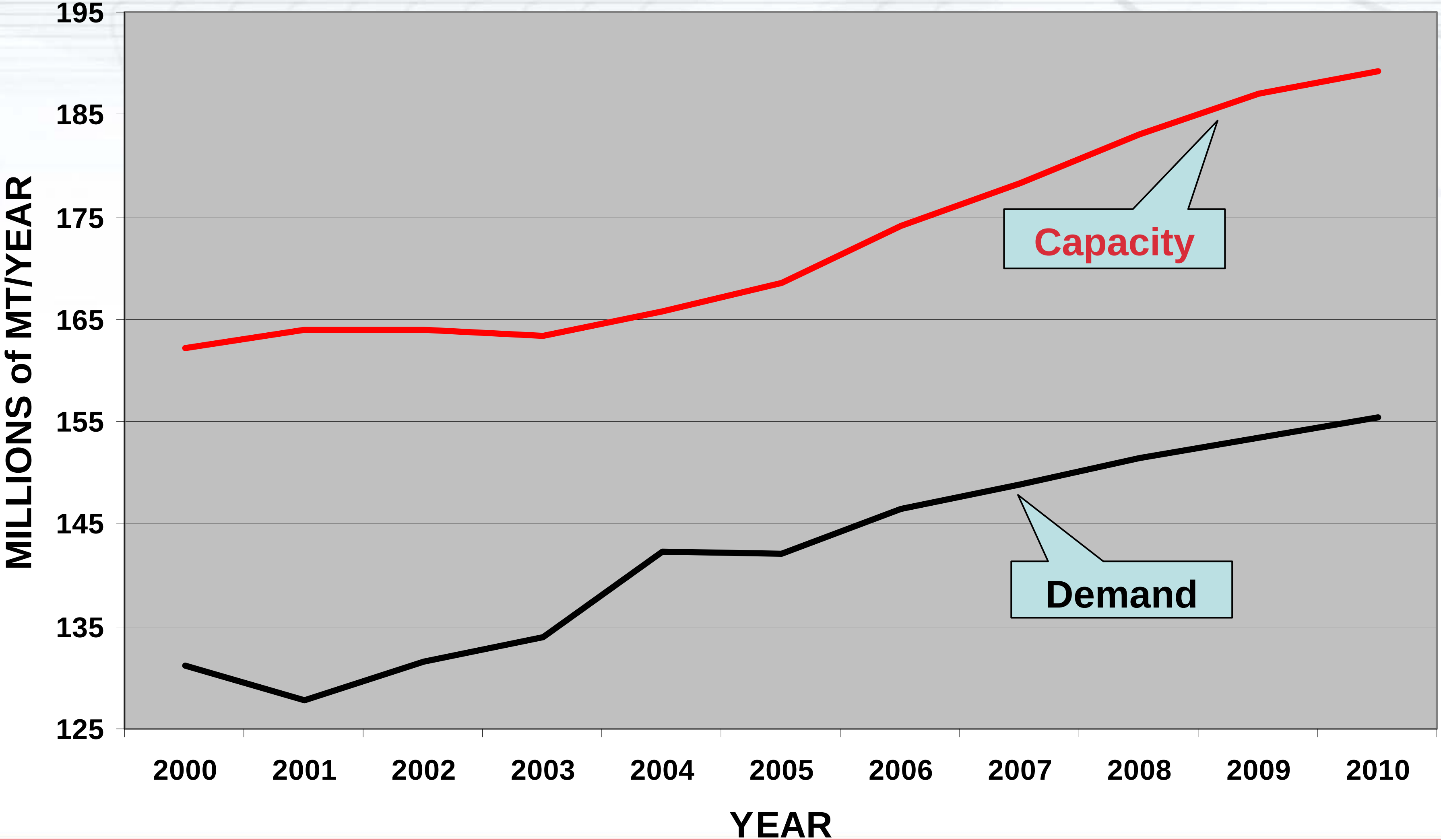
World Ammonia Capacity
(Source – Fertecon)



World Ammonia Capacity & Demand

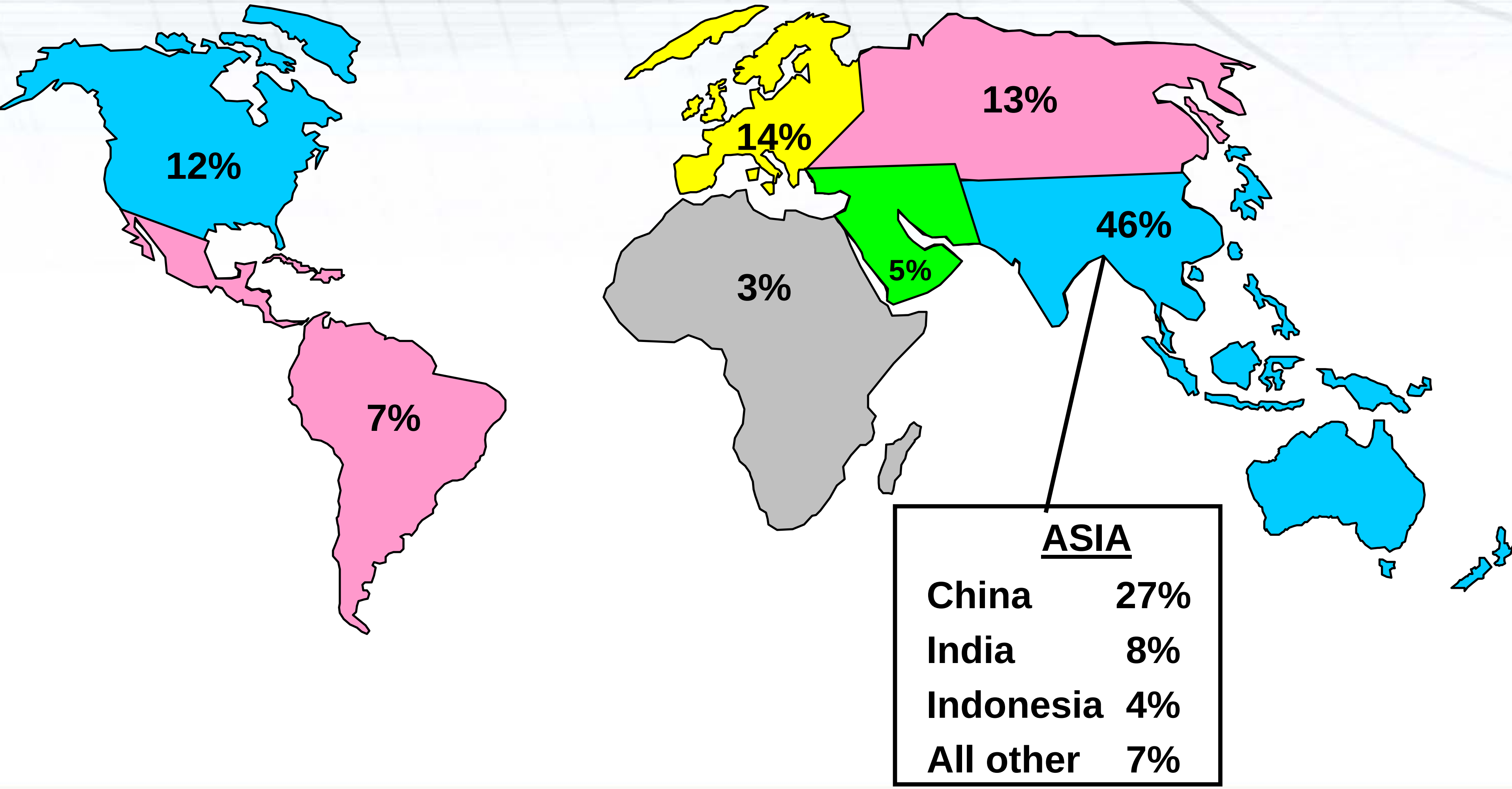
(Source-Fertecon)



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

Ammonia Plant Capacity by Region



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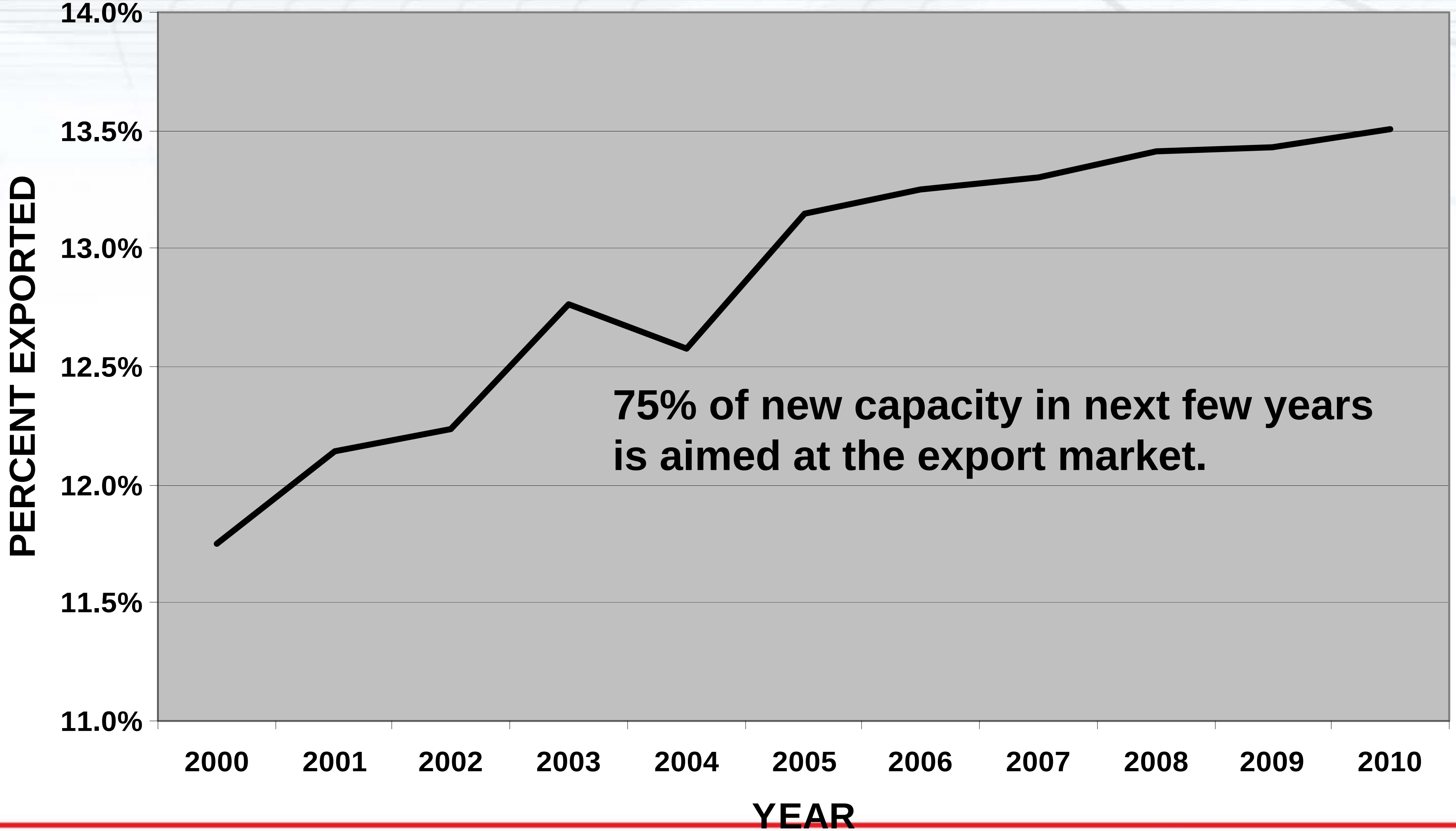
Trends in World Ammonia Exports
(Percent of World Production)



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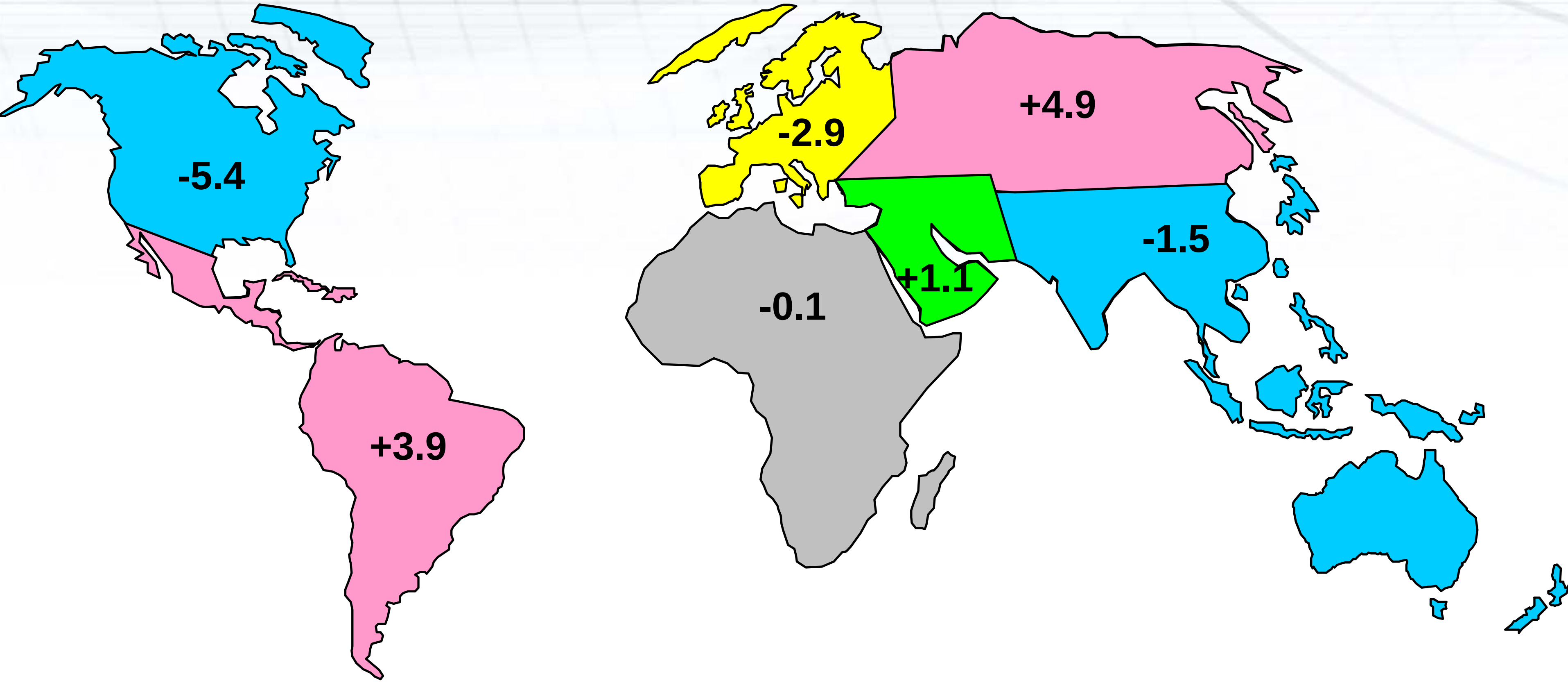
Net World Ammonia Trade in MM MT/Year

(Plus=export, minus=import)

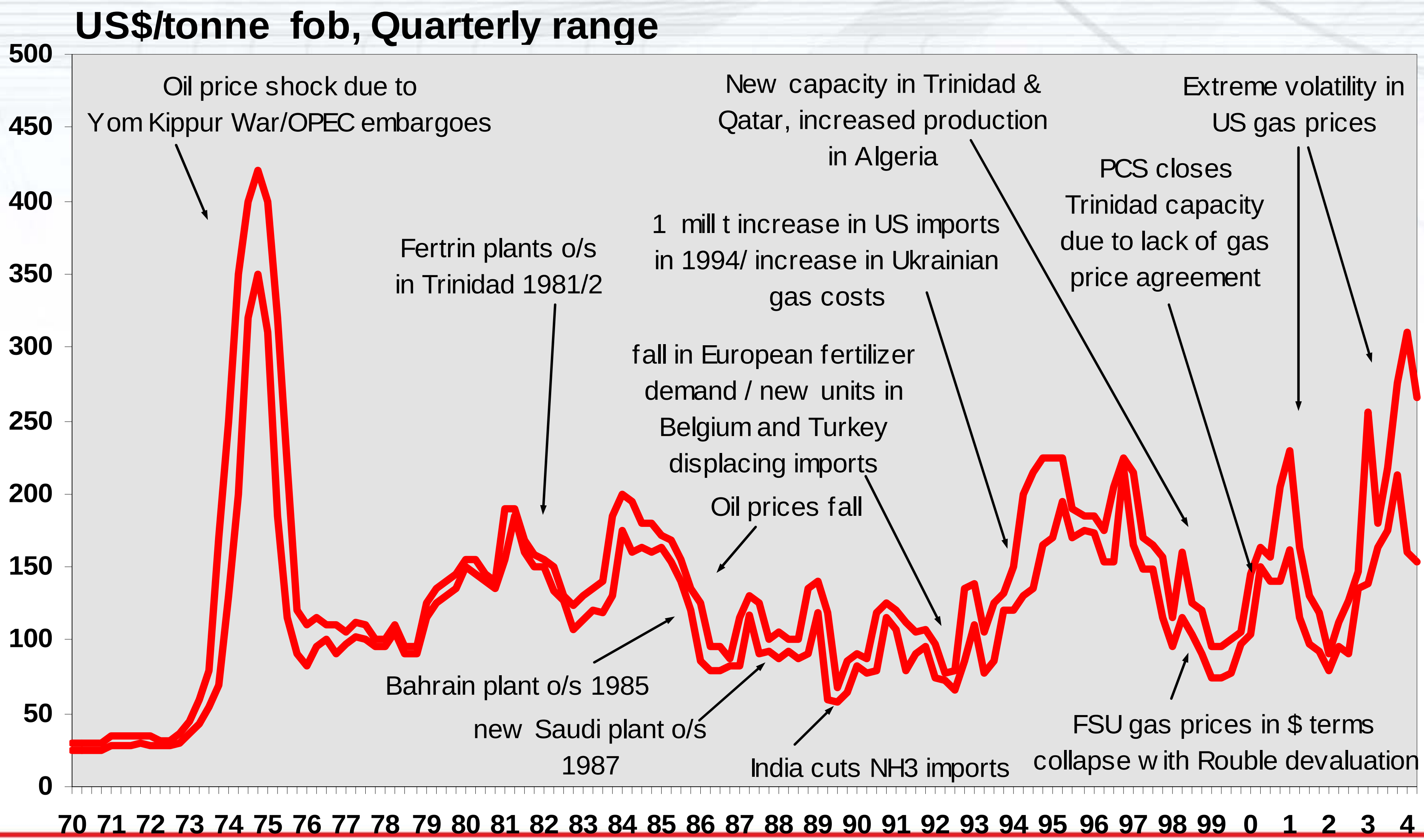


Total trade in 2004 = 17.9 mt (Fertecon)

Net trade in 2004 = 9.9 mt (Estimate)

Historical US Gulf Coast NH_3 Prices

(Fertecon, current dollars)



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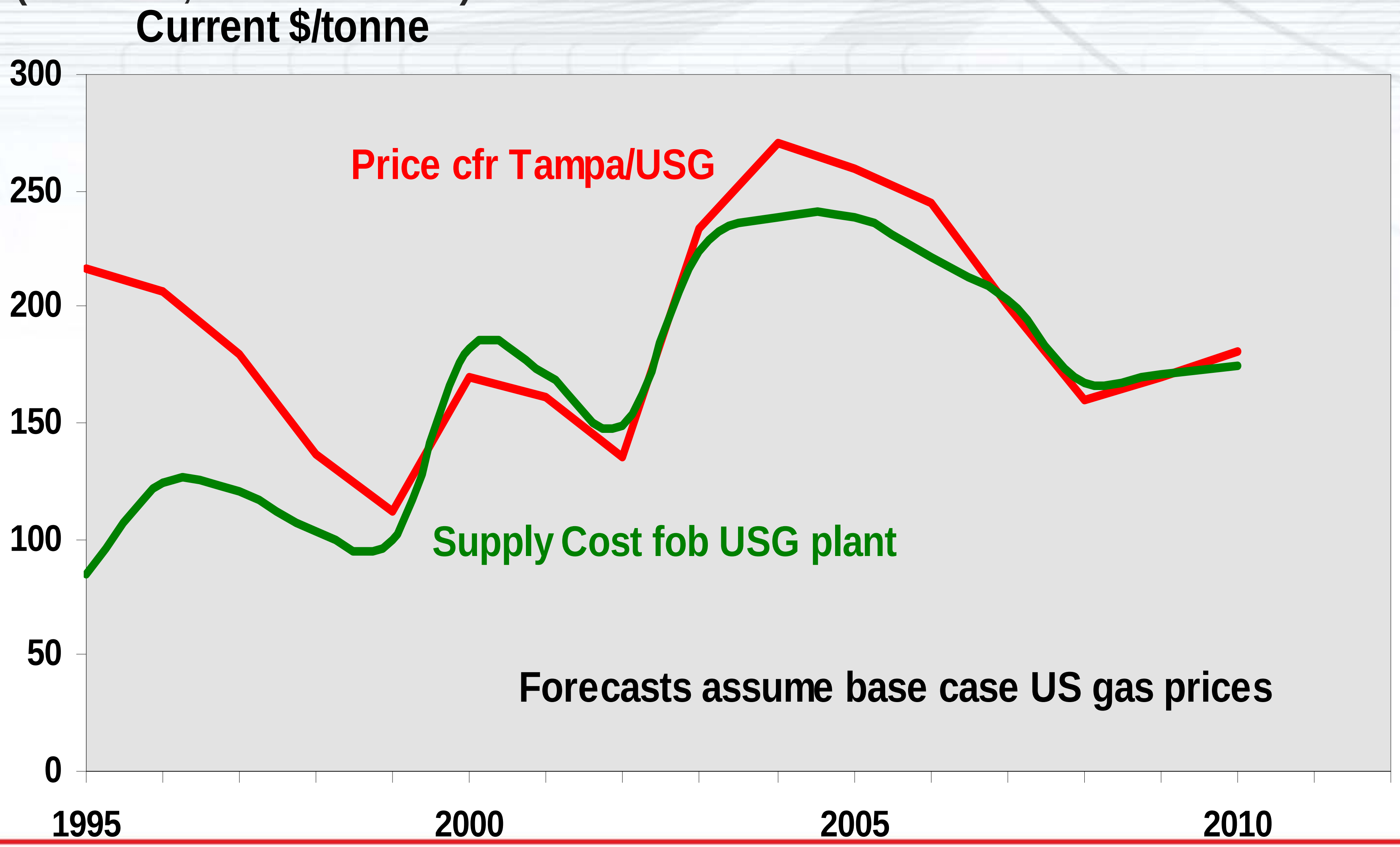
Predicted US Gulf Coast NH_3 Prices

(Fertecon, current dollars)



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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

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

- Recognized as an element in 1766 by Henry Cavendish

- Named by Antoine Lavoisier in 1783 after he discovered its ability to generate water

$$2H_2 + O_2 \rightarrow 2\,H_2O$$

History of Hydrogen Production

- First commercial production in early 19th century making town gas from coal

$$\text{Coal} + H_2O \rightarrow H_2 + CO + CH_4$$

- In early 20th century, coke and coal were gasified with either air or oxygen to produce H_2 + CO mixtures for chemical synthesis

- First steam-methane reformer on-line in 1931

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

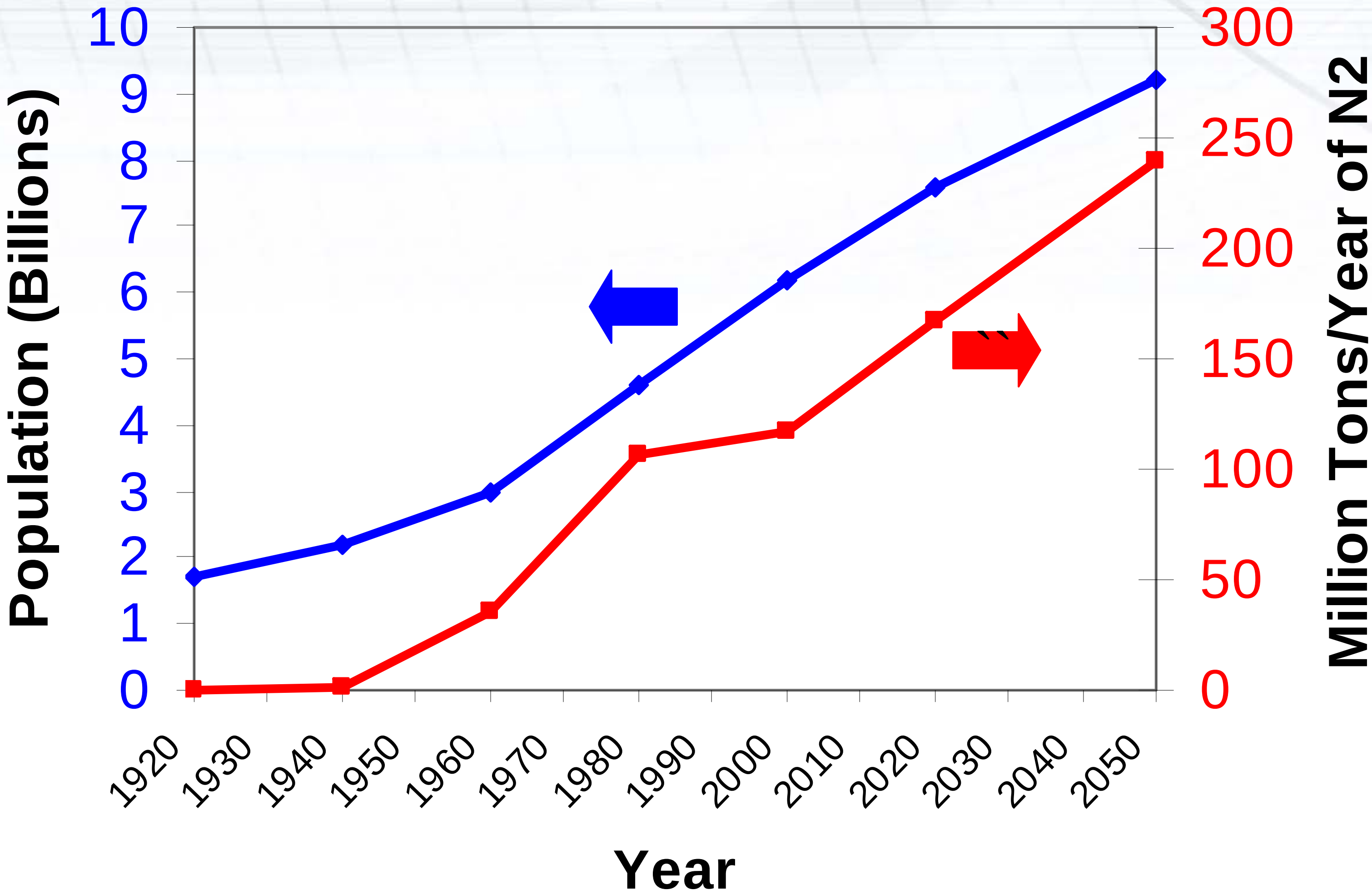
Hydrogen Sources for Making Ammonia

Process	Reaction	Approximate Relative Energy Consumption
Water electrolysis	$2H_2O \rightarrow 2H_2 + O_2$	300%
Coal gasification	$C + 2H_2O \rightarrow 2H_2 + CO_2$	170%
Heavy fuel oil	$CH + 2H_2O \rightarrow 2\frac{1}{2}\ H_2 + CO_2$	135%
Naphtha reforming	$CH_2 + 2H_2O \rightarrow 3H_2 + CO_2$	104%
Nat. gas reforming	$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	100%

History of Ammonia Manufacture

	YEAR
Ammonia consists of hydrogen & nitrogen	1784
First equilibrium test by Haber	1904
Haber patent	1908
Catalyst program by Haber & BASF	1908 - 1922
Equipment program begun by Bosch at BASF	1910
First commercial plant - 30 mt/d at BASF	1914
World capacity reaches 2000 mt/d	1927
World capacity reaches 450,000 mt/d	2005

World Population & NH_3 Production Trends



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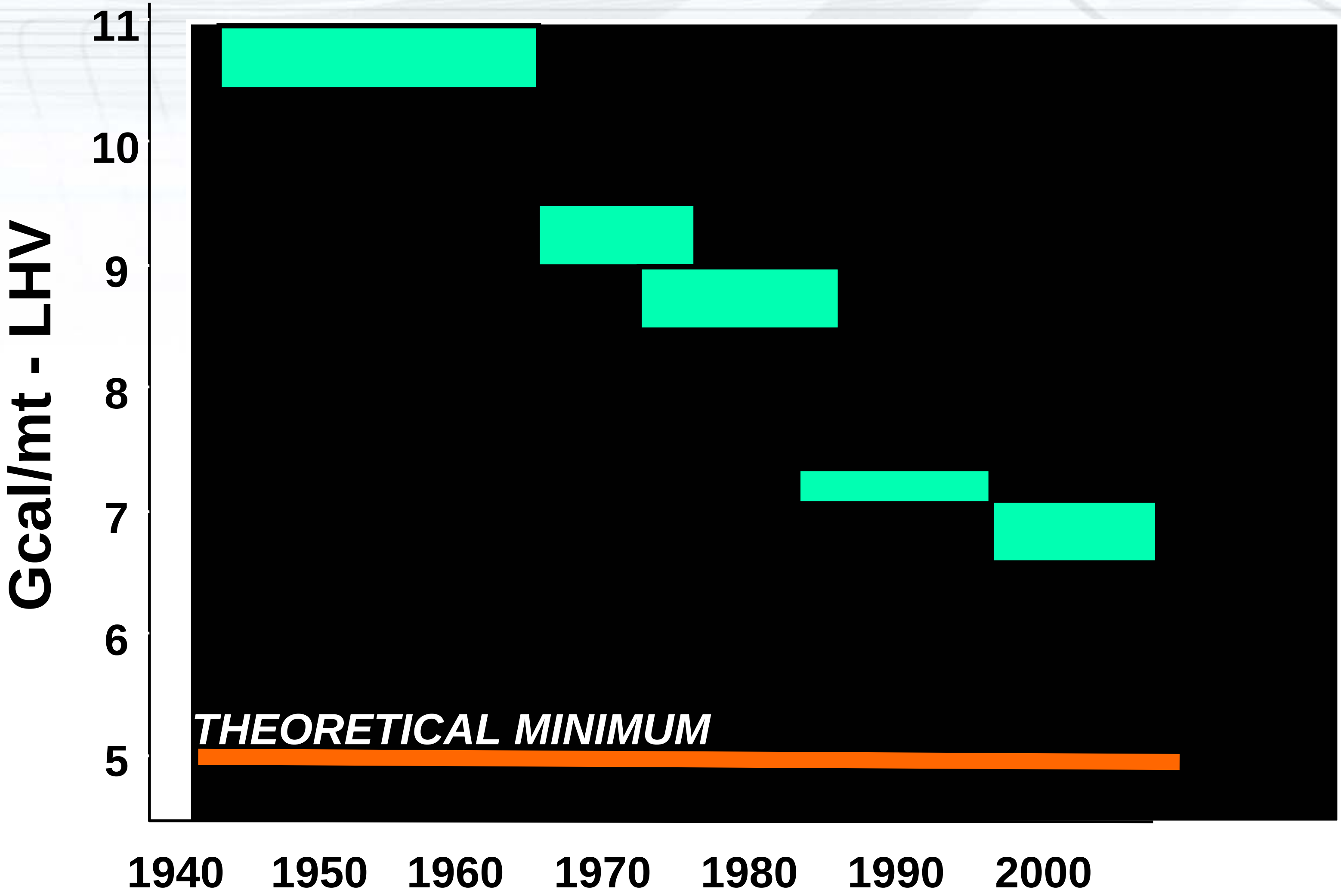
Market Situation – Old Plants

- **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**

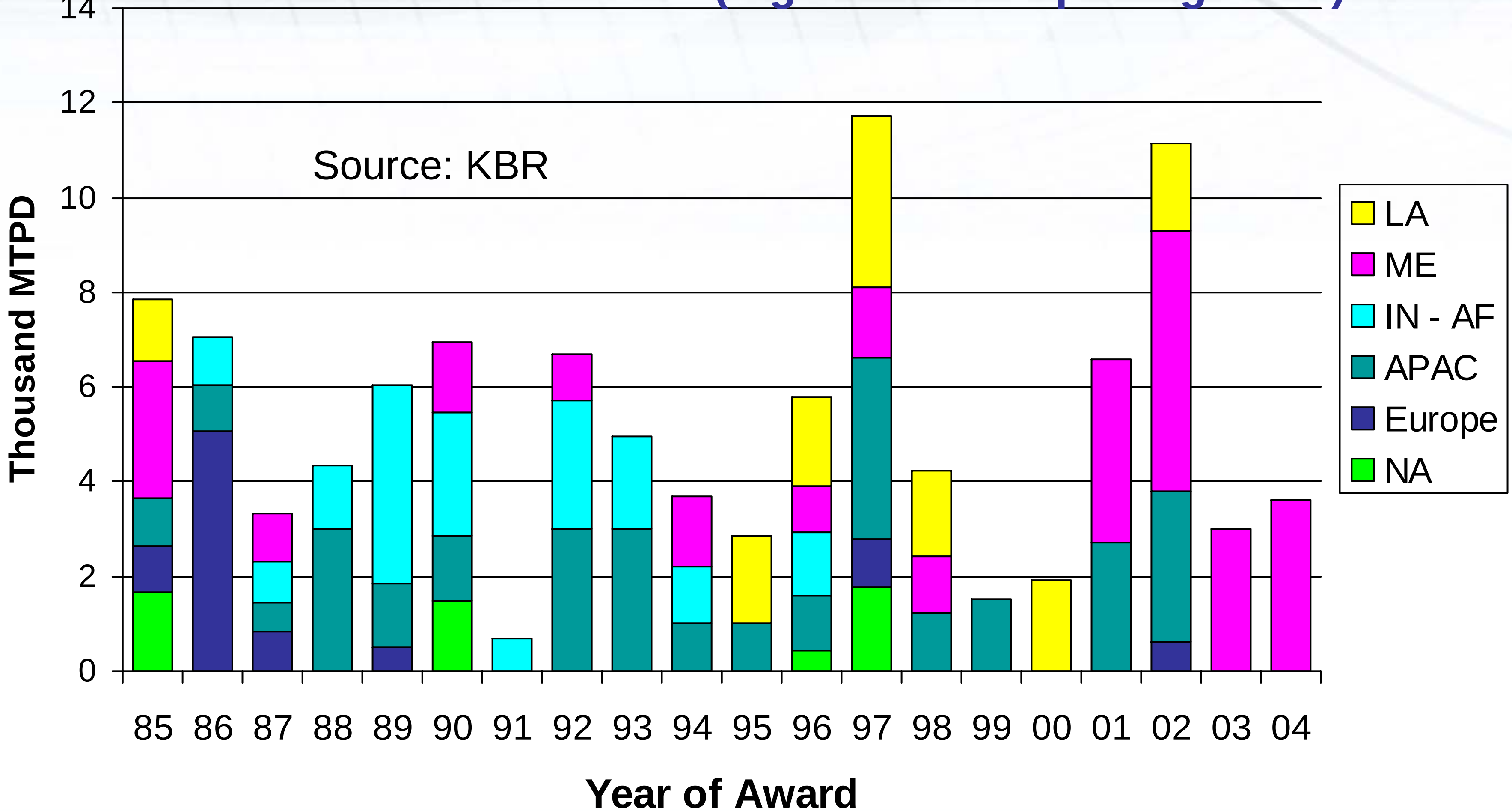
- **Many operators debottleneck existing capacity to improve economy of scale**

New Plant Trends in Energy Consumption



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)



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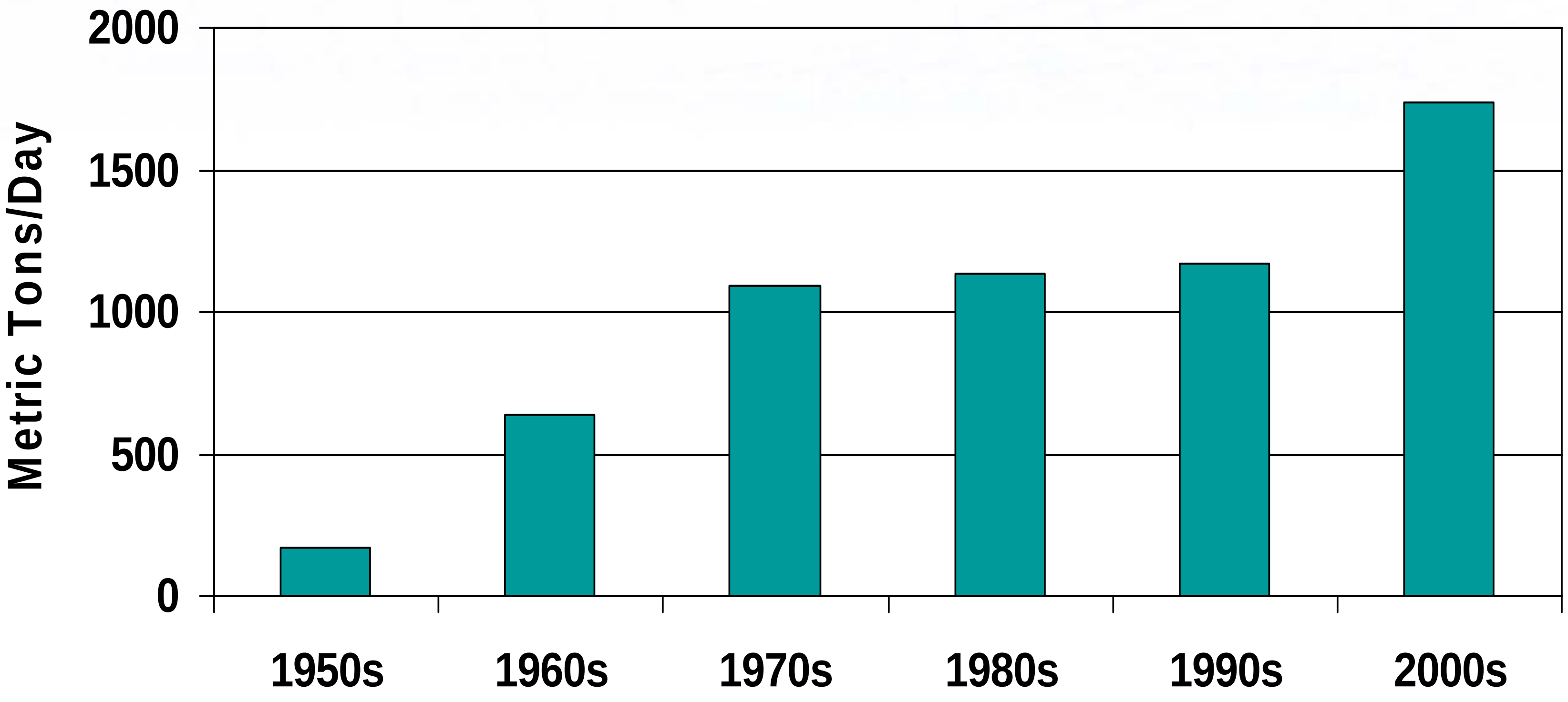
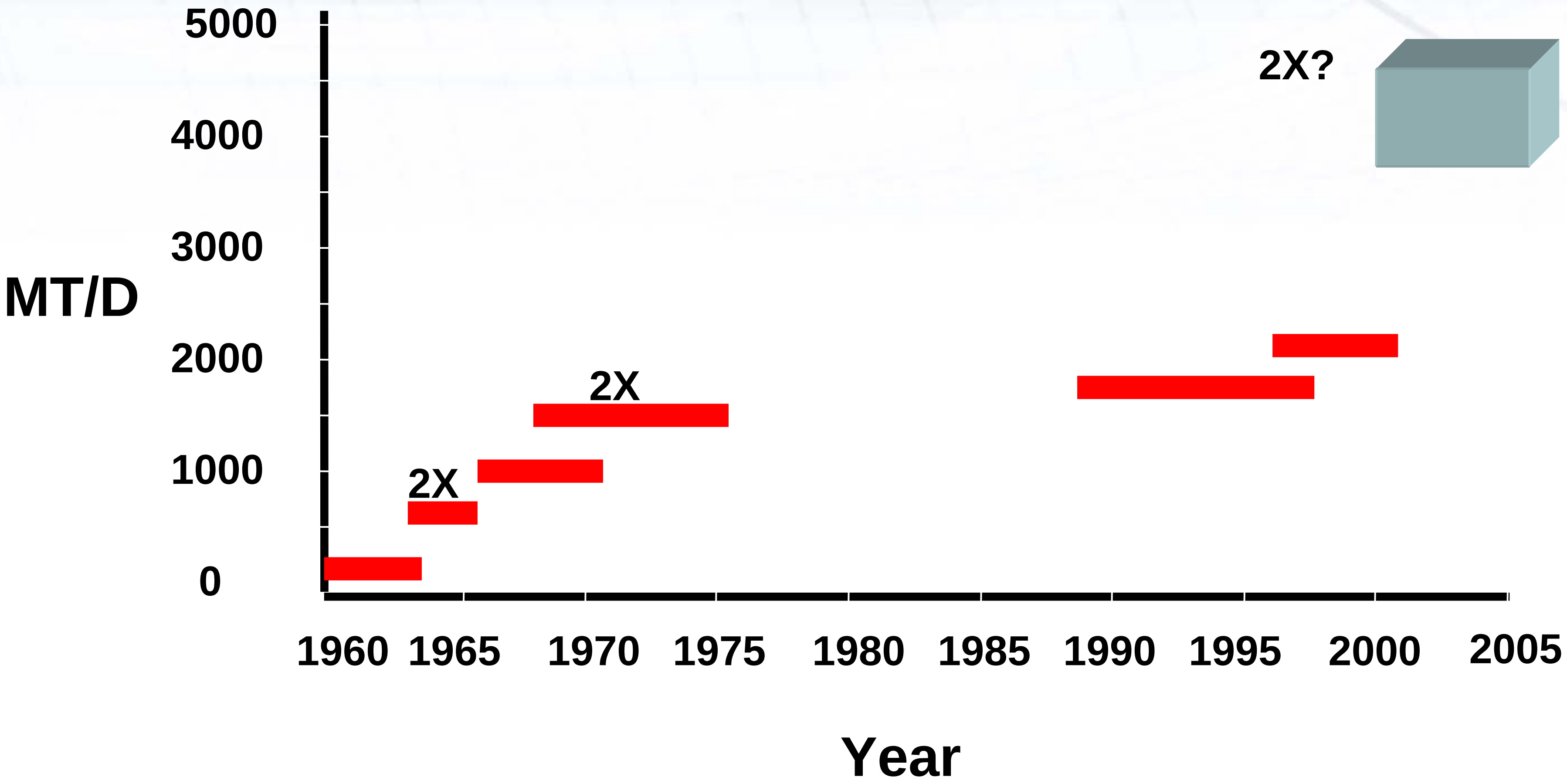
Average Capacity Built by Decade

KBR Licensed Plants

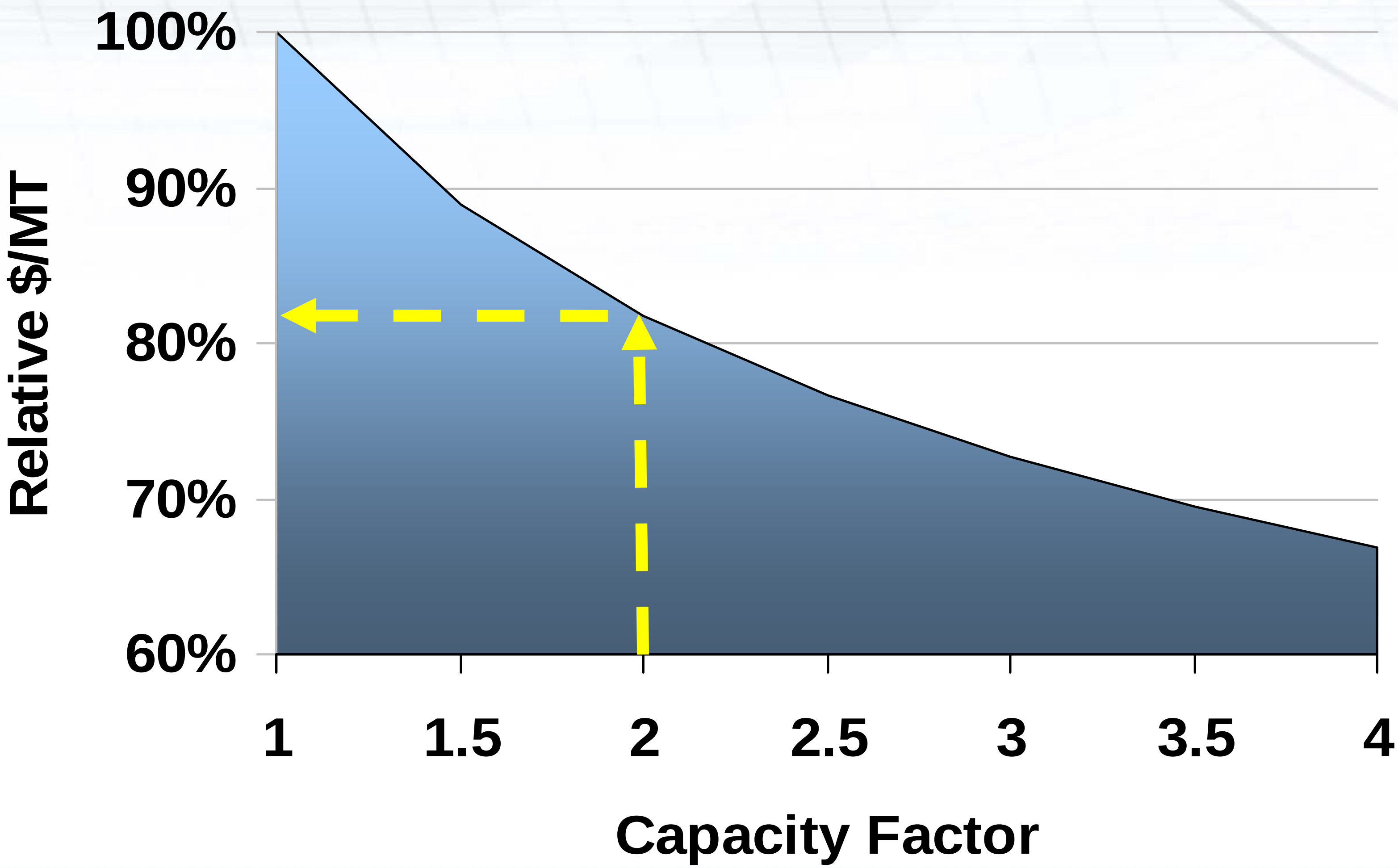


History of Maximum Size NH_3 Plants



Indicative Capital Cost

(Assumes 0.7 exponent)



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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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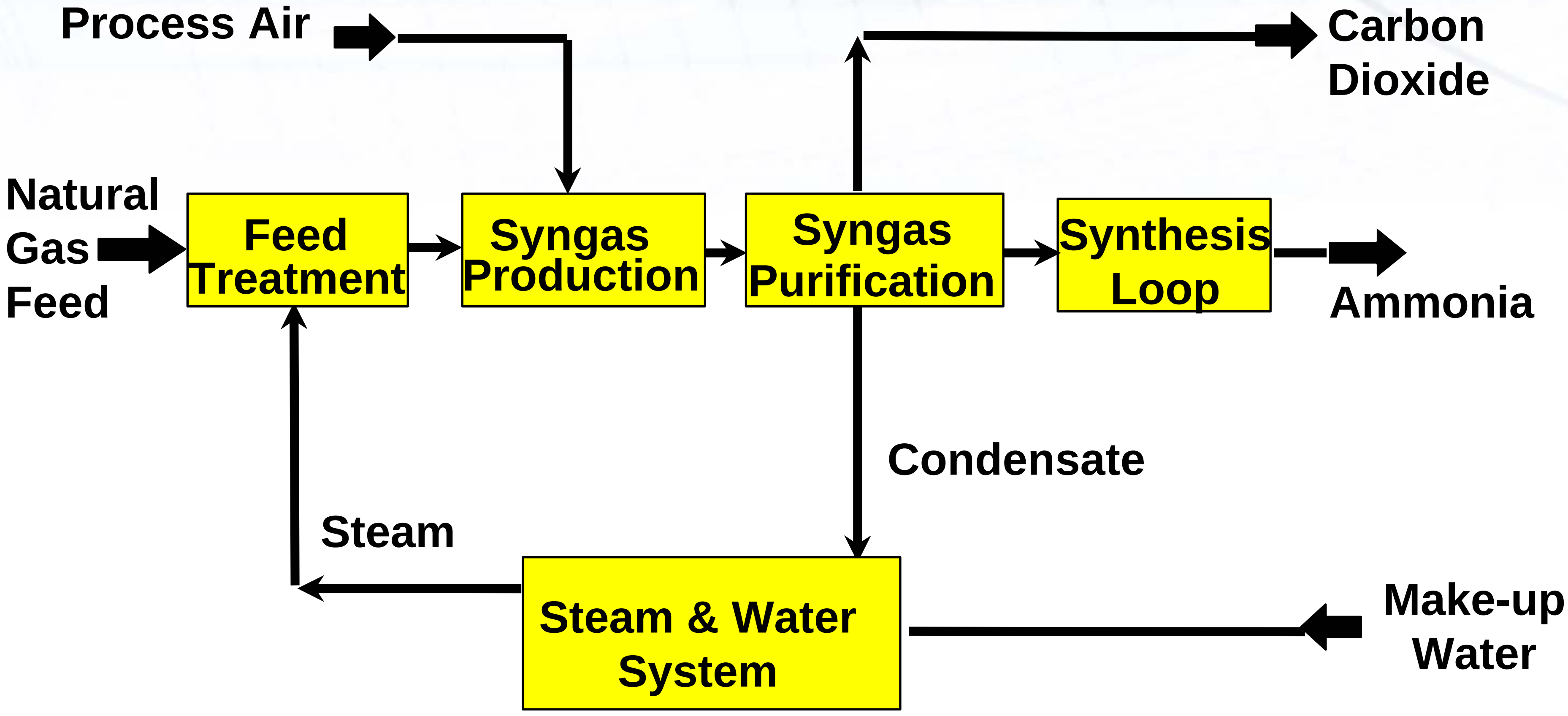
Sections in an Ammonia Plant



Chemistry of Syngas Production

Process	Chemical Reaction	Favorable Conditions
Primary Reforming	heat + $CH_4 + H_2O \rightarrow 3H_2 + CO$	High temp & High stm/carbon
Secondary Reforming	$O_2 + 2H_2 \rightarrow 2H_2O$ + heat heat + $CH_4 + H_2O \rightarrow 3H_2 + CO$	High temp & High stm/carbon
High temp shift	$CO + H_2O \rightarrow CO_2 + H_2$ + heat	Low temperature High steam/CO
Low temp shift	$CO + H_2O \rightarrow CO_2 + H_2$ + heat	Low temperature High steam/CO

Engineering of Syngas Production

Process	Equipment	Features
Primary Reforming	Catalyst-packed tubes in a furnace	Nickel catalyst
Secondary Reforming	Refractory-lined pressure vessel	Nickel catalyst
High temp shift	Pressure vessel	Iron-chrome catalyst
Low temp shift	Pressure vessel	Copper-zinc catalyst

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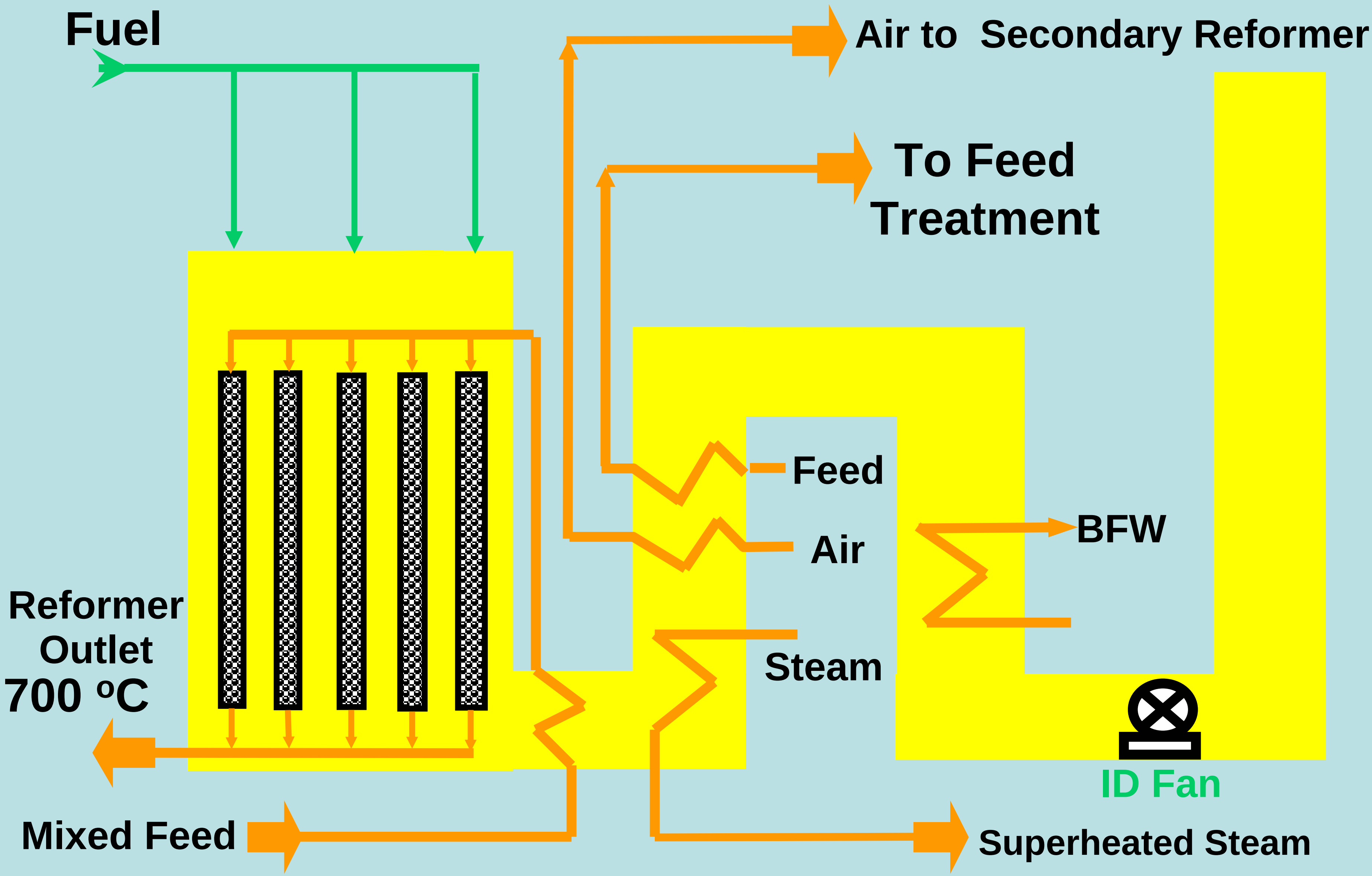
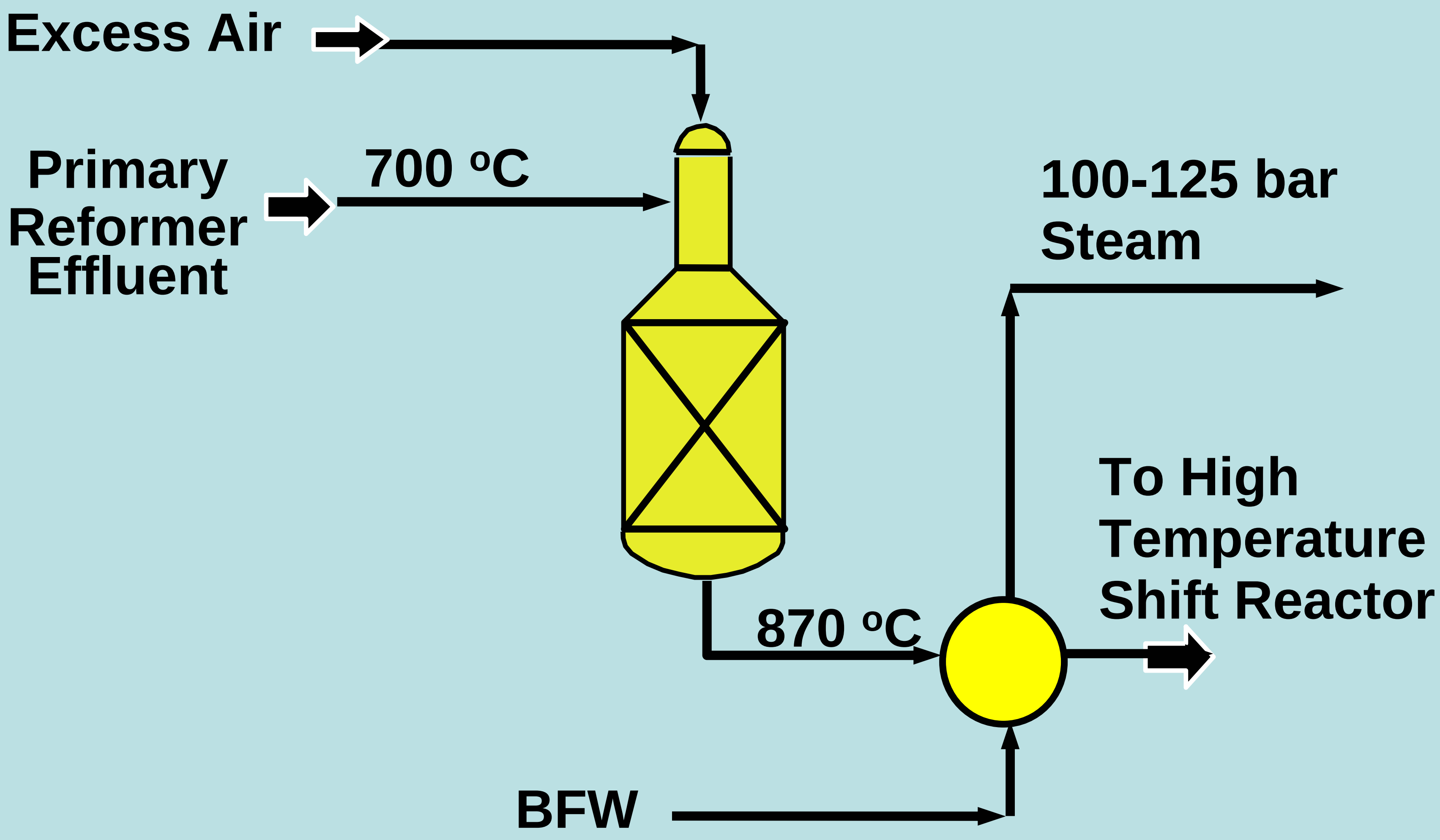
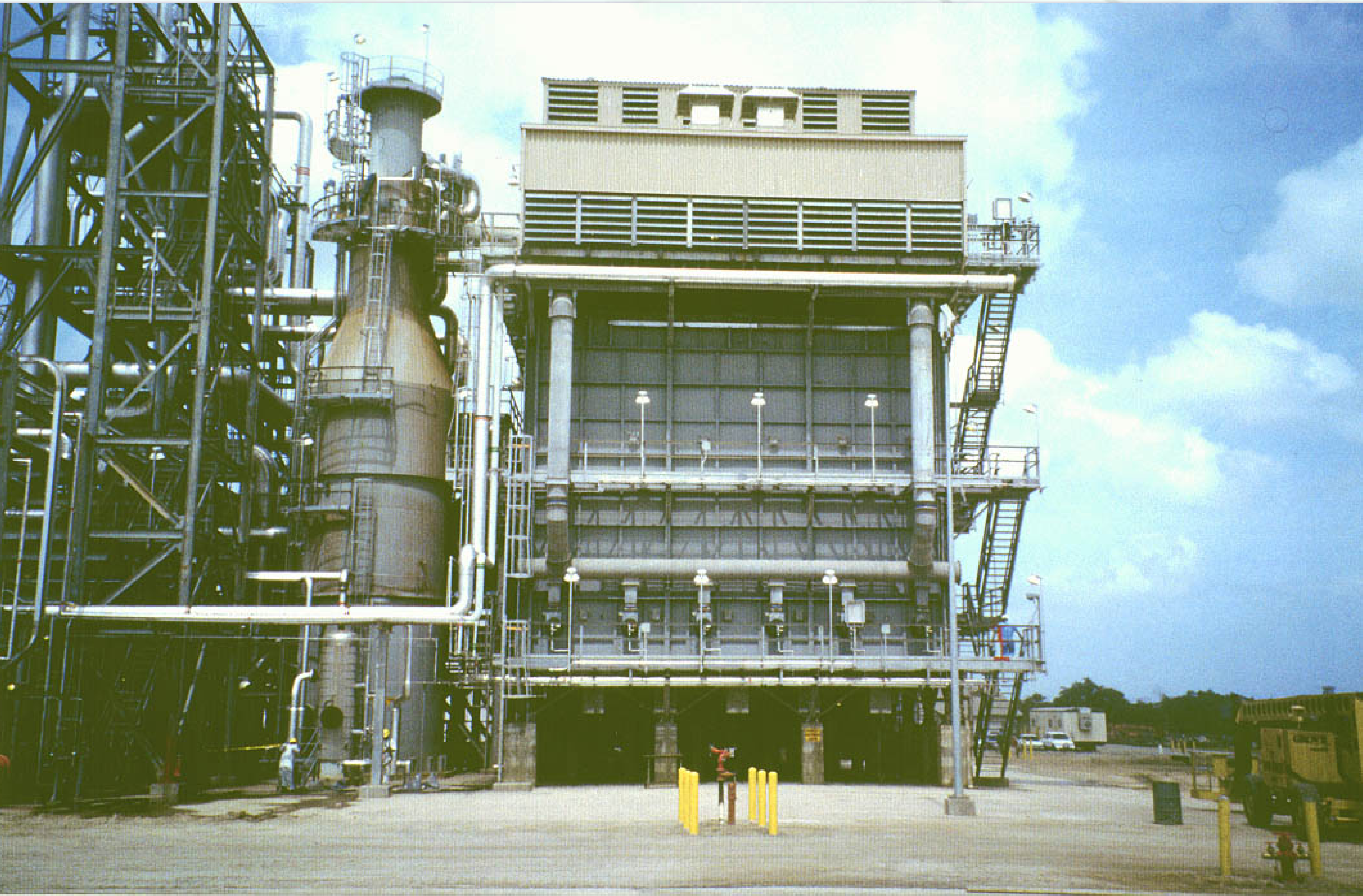
Primary Reforming



Secondary Reforming

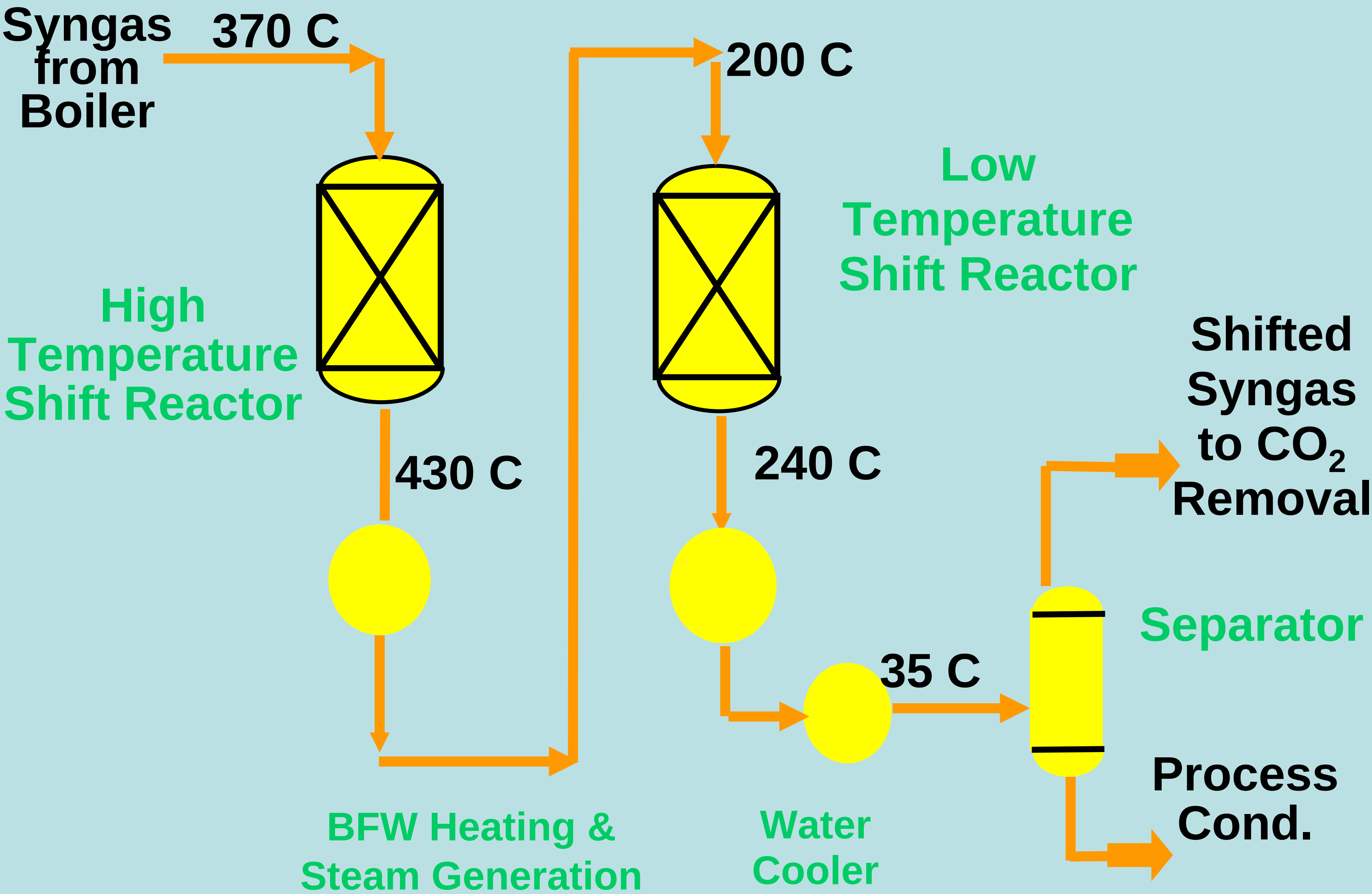


Primary & Secondary Reformers



Primary Reformer with Gas Turbine

Shift Conversion



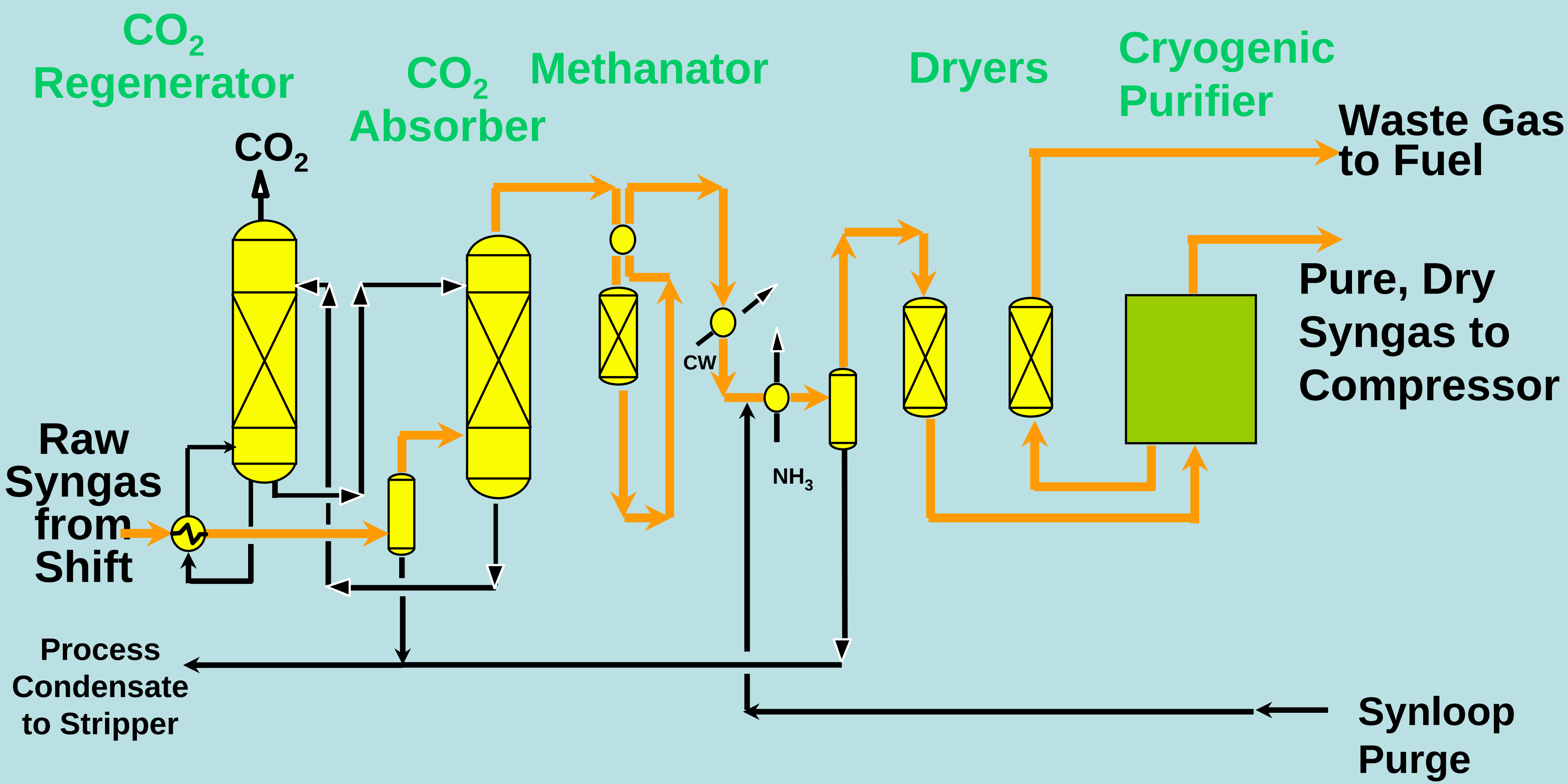
Chemistry of Syngas Purification

Process	Description	Favorable Conditions
CO_2 Removal	Physical Dissolution or Chemical Reaction	Low temp & High pressure
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$ $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	280 - 350°C
Drying	Physical Adsorption to remove water & CO_2	2 - 4 °C
Cryogenic Purification	Separation of argon, residual CH_4 and excess N_2 from syngas	-180 °C

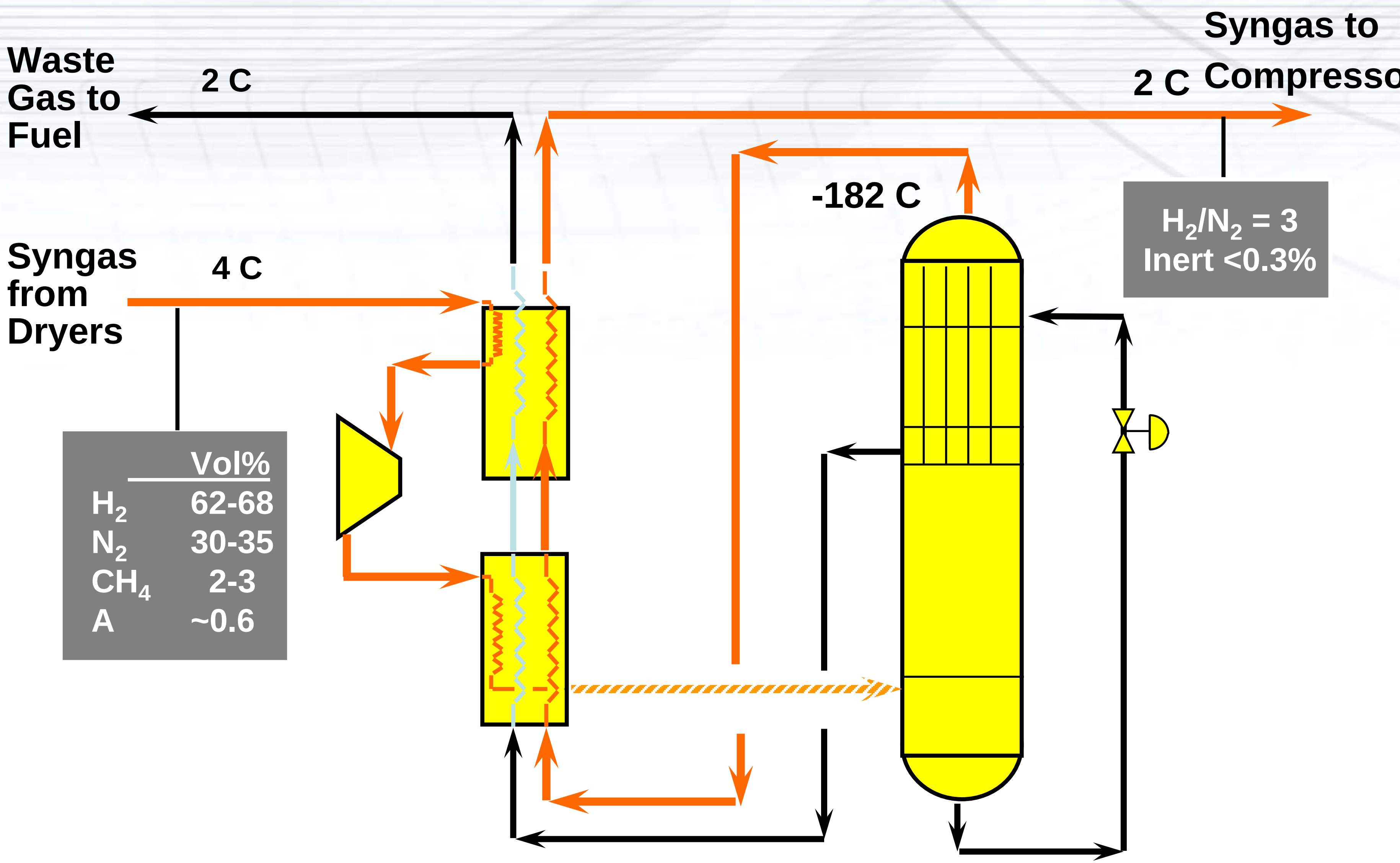
Engineering of Syngas Purification

Process	Equipment	Features
CO_2 Removal	Absorb/regen columns with solution circulation pumps	Contact syngas with solution over packing
Methanation	Pressure vessel	Nickel catalyst
Drying	Two pressure vessels each with a filter	Cyclic operation of mol sieve desiccant
Cryogenic Purification	Plate fin exchanger, expander, column	Aluminum, generator brake, trays, set H/N = 3.0

Syngas Purification



KBR Cryogenic Purifier



CO_2 Removal System

1500 t/d plant in China

KBR Cryogenic Purifier

1850 t/d plant in Holland

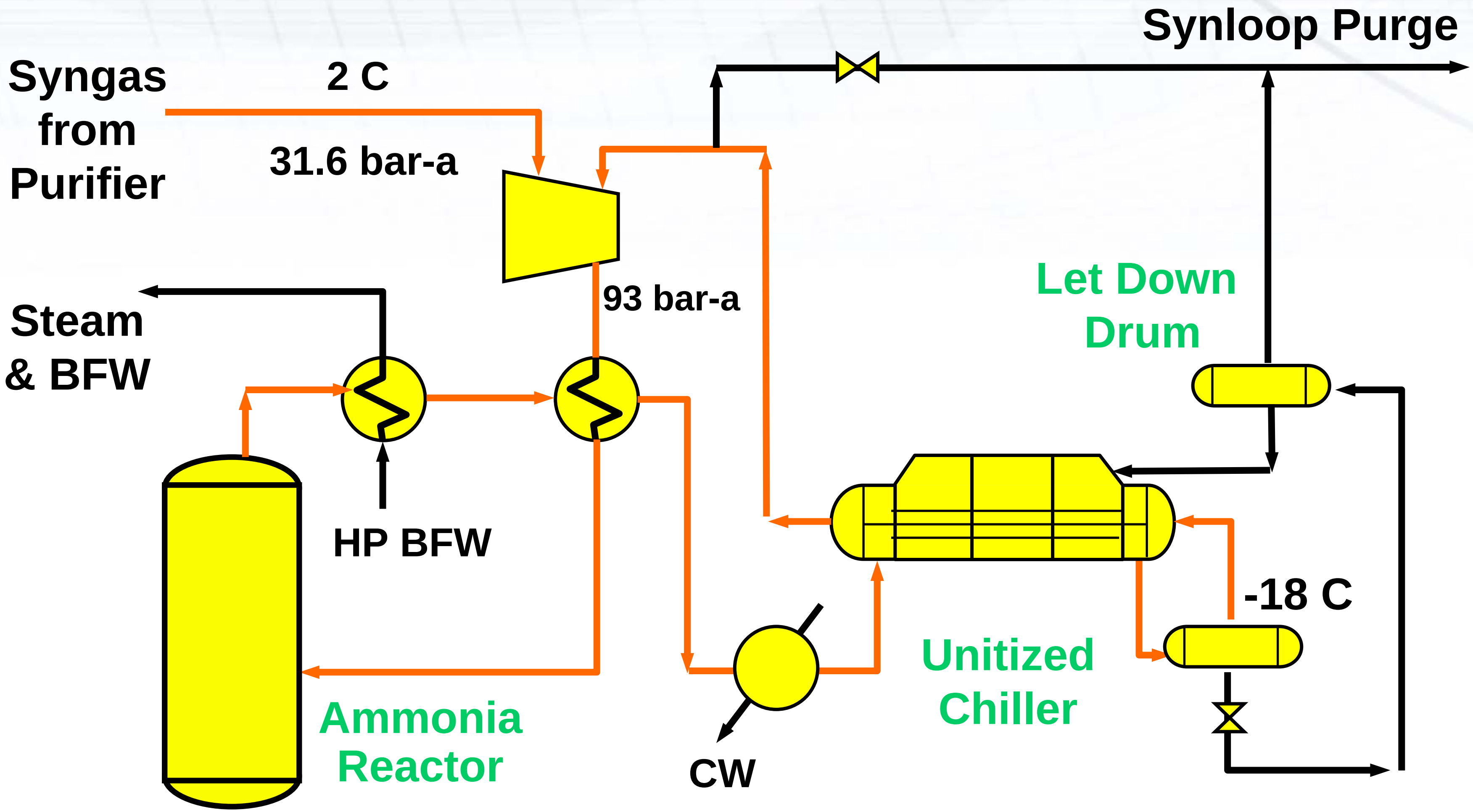
Chemistry of Ammonia Synloops

Process	Description	Favorable Conditions
Synthesis	$3H_2 + N_2 \rightarrow 2NH_3$ + heat	Low T & high P
Heat Recovery	Generate 100 bar+ steam	High T
Product Recovery	Condense via refrigeration	Low T & High P

Engineering of Ammonia Synthesis

Process	Equipment	Features
Synthesis	Catalyst filled pressure vessel	P = 90 – 175 bar T = 400 - 500 C
Heat Recovery	Shell & tube heat exchanger	Proprietary design
Product Recovery	Compression refrigeration system	Ammonia as the refrigerant

Ammonia Synthesis Loop



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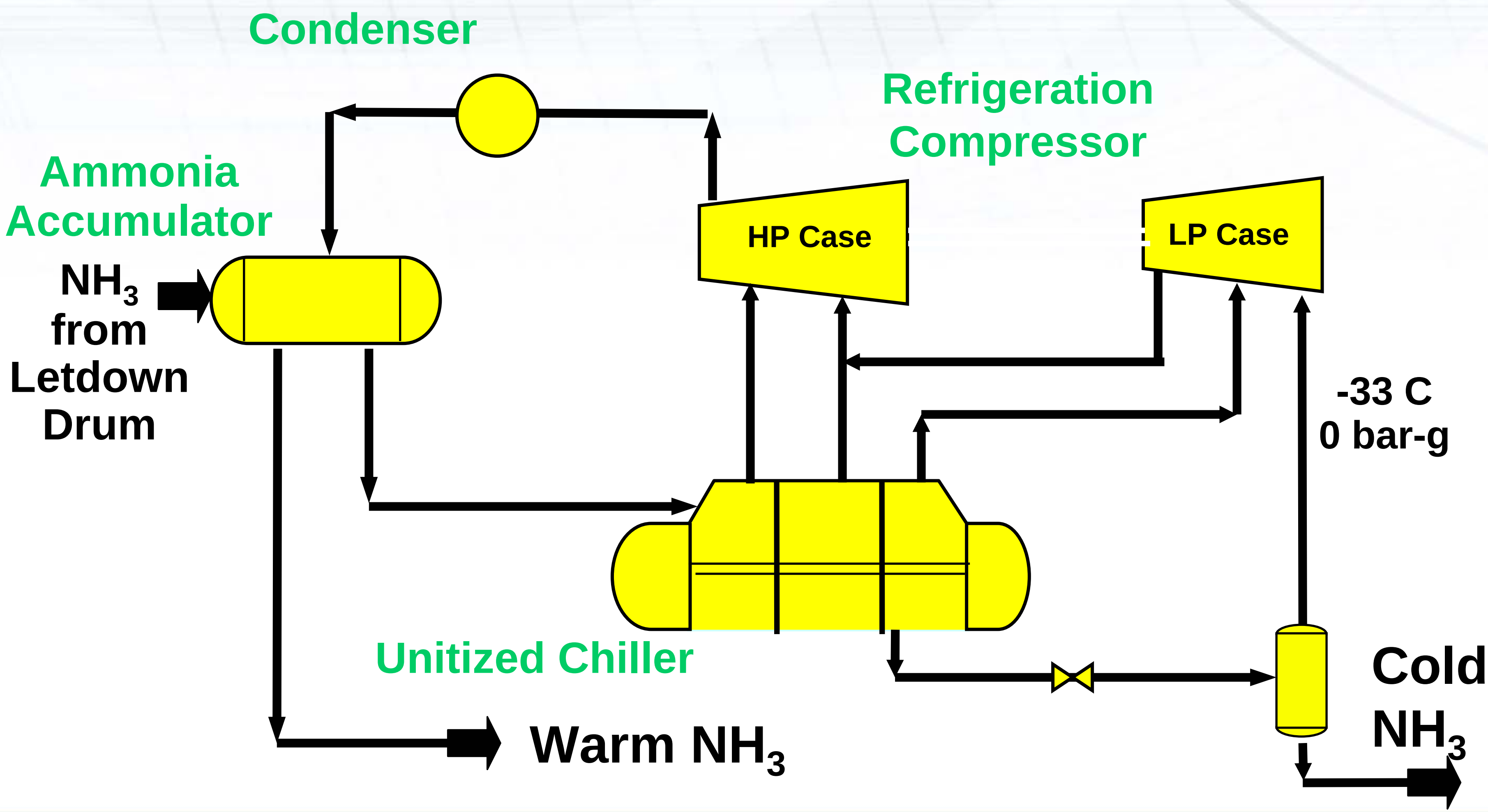
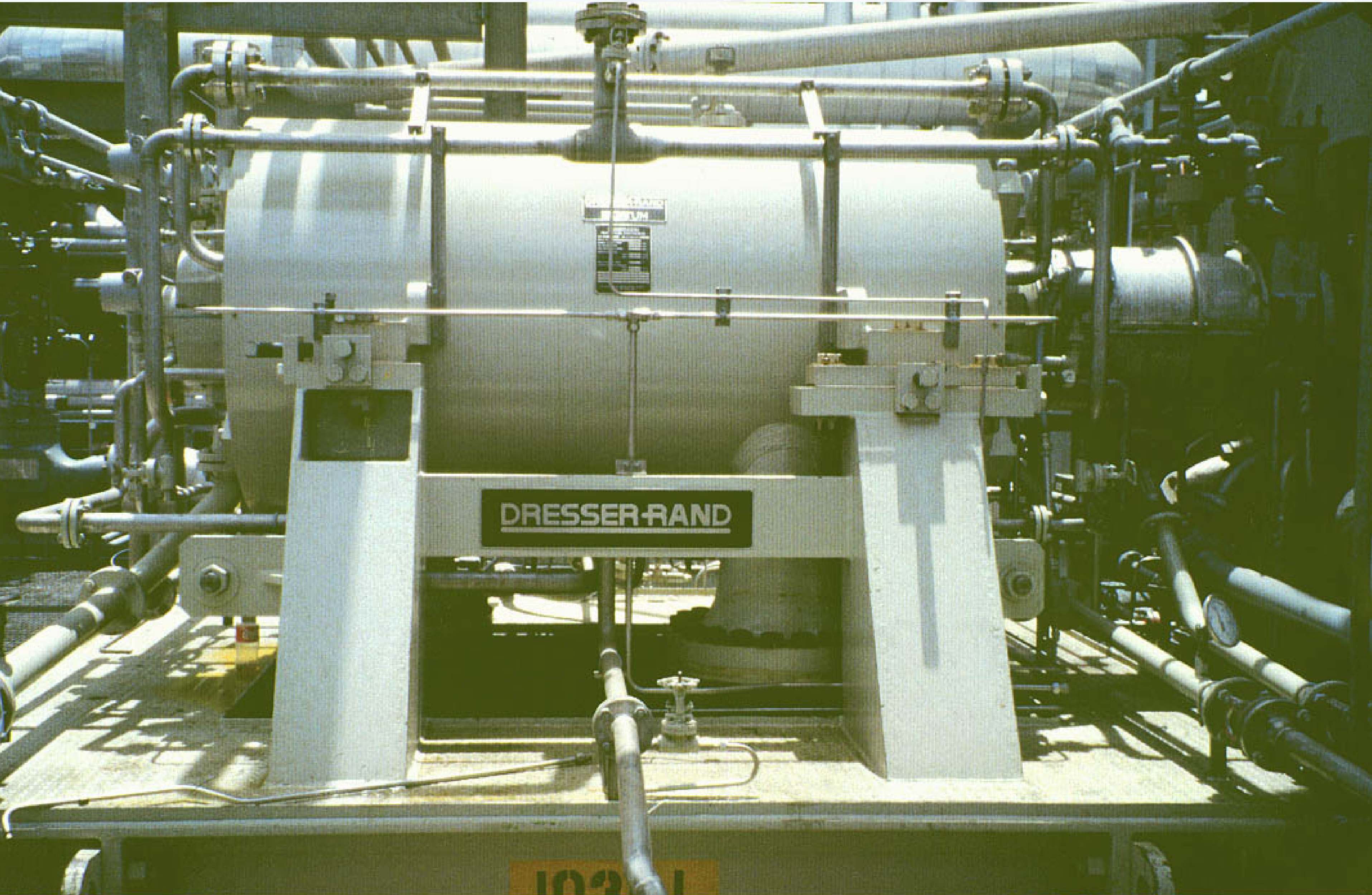
Refrigeration System



Single-case Synthesis Gas Compressor



Ammonia Converter

KAAP Catalyst

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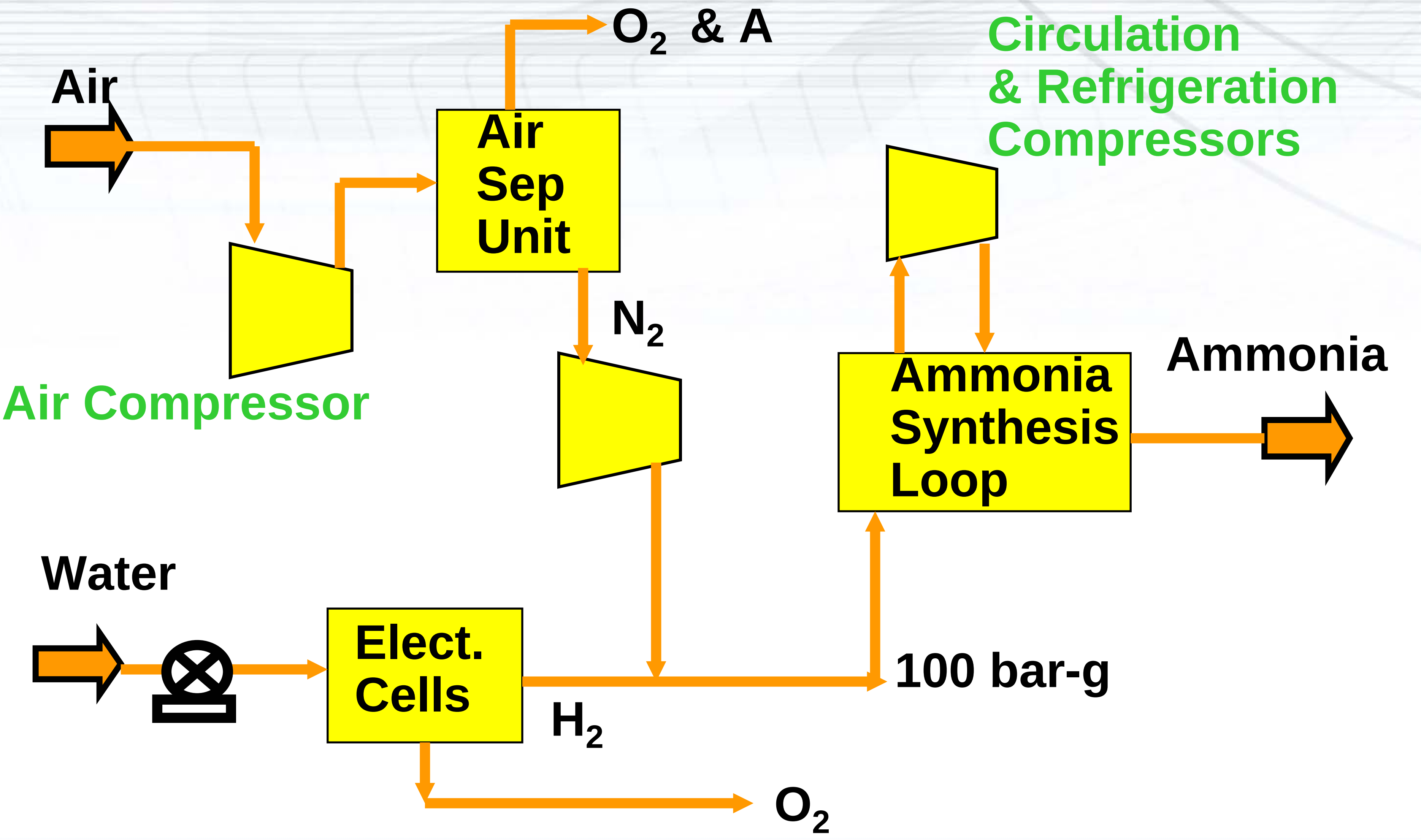
Ammonia from Water Electrolysis
Conceptual Process Scheme



Material Balance

(tons/ton of ammonia – assumes no losses)

	IN	OUT
Air	1.09	
Water	1.59	
Ammonia		1.00
Oxygen		1.67
Argon		0.01
TOTAL	2.68	2.68

Electric Power Input to Process

	kWh/MT of NH_3
Compressors	390
Pump	8
Electrolytic cells	7000 – 9000 [1]
TOTAL	~7400 – 9400

(1) Based on 3.5 – 4.5 kWh/Nm^3 of H_2

Approx. Energy Consumption of Process

	GCal/MT of NH_3
Electricity @ 860 kcal/kWh	6.4 – 8.1[(1)]
Heat recovery from loop	-0.6
TOTAL	5.8 – 7.5

(1) Based on 3.5 – 4.5 kWh/Nm^3 of H_2

Approx. Energy Consumption (Cont'd)

	Gcal/Metric Ton NH_3	
	860 kcal/kWh	2150 kcal/kWh(2)
Electricity (1)	6.4	16.0
Heat recovery	-0.6	-0.6
TOTAL	5.8	15.4

(1) Based on 3.5 kWh/Nm^3 of H_2

(2) Conversion of primary energy to electricity at 40% efficiency.

Approx. Variable Operating Cost

	$/MT of NH_3
Electricity @ $0.035/kWh	$259 (1)
Water @ $5/1000 gallons	2
By-product O_2 @ $25/t	-42
Heat recovery @ $40/Gcal	-24
TOTAL	$195

(1) Based on 3.5 kWh/Nm^3 of H_2

NH_3 as Auto Fuel –Supply & Demand

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

- Daily US demand for gasoline
  - Is about 9×10^6 barrels[(1)]
  - Corresponds to about 47×10^6 million Btu

(1) US DOE, EIA

Ammonia as Auto Fuel

- Fuel Price Comparison
  - NH_3 @ $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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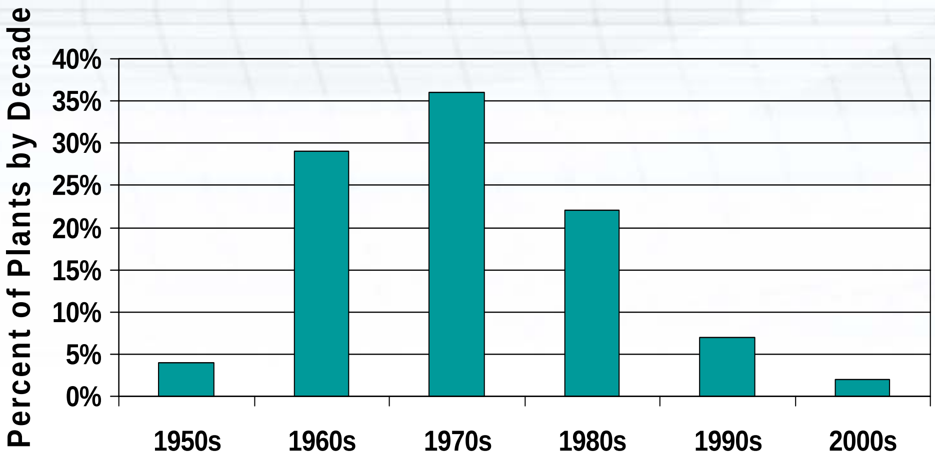
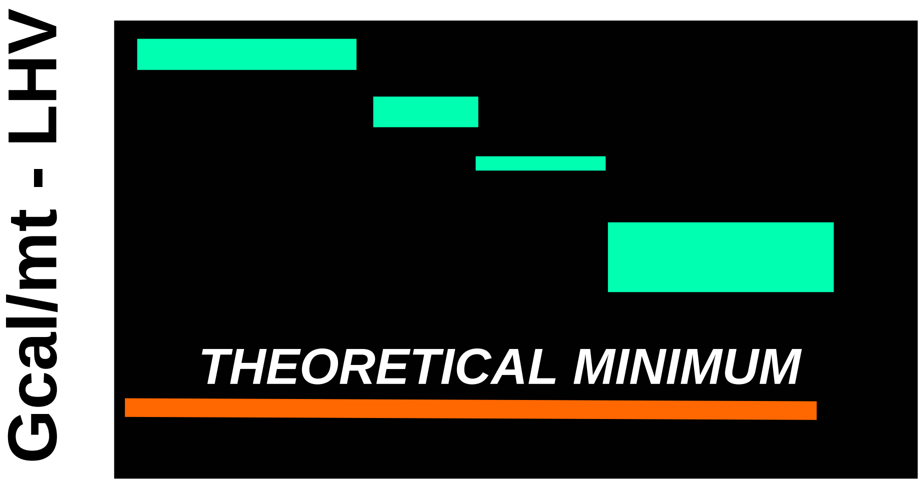
Ammonia Technology Summary

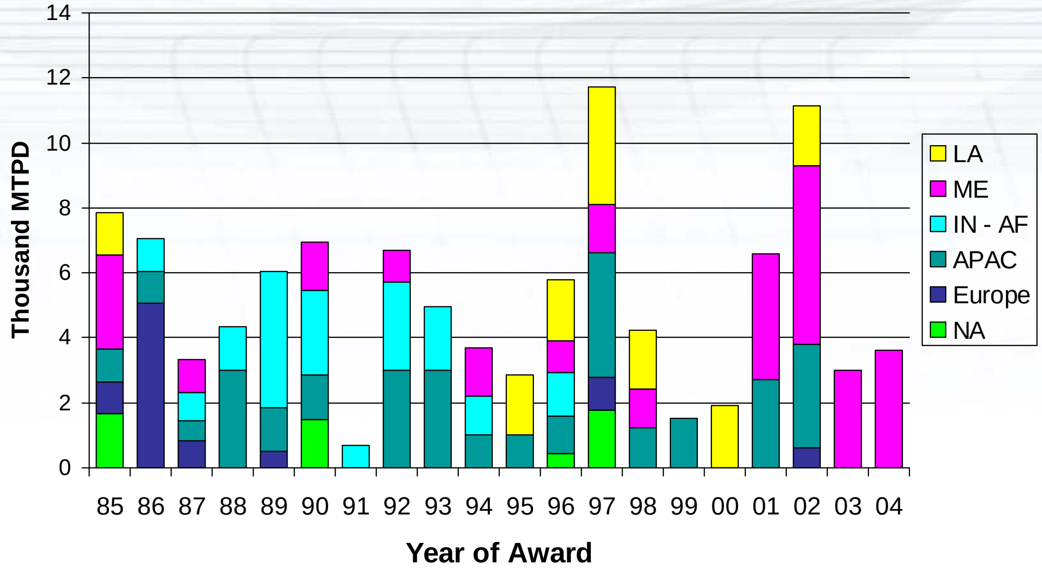


1970s – a decade of rapid capacity expansion

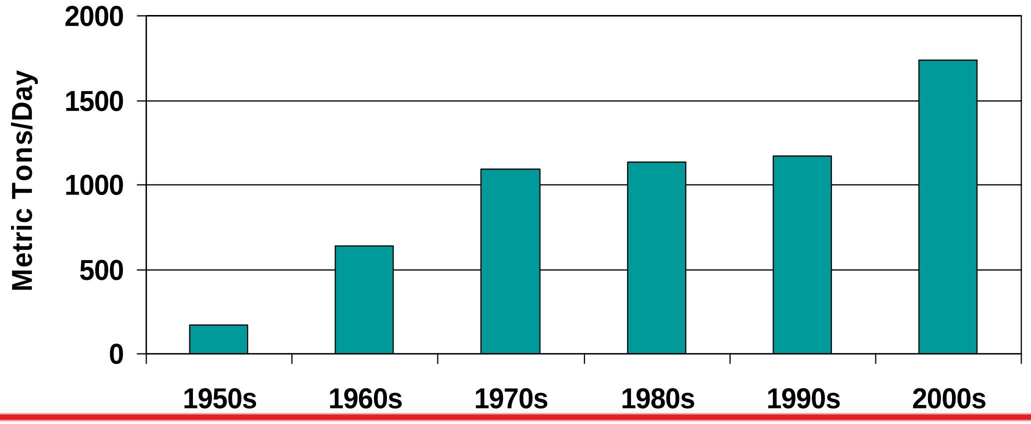


1980s – a decade of reduced energy consumption

Ammonia Market Summary



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



2000s – a decade of increased plant capacities

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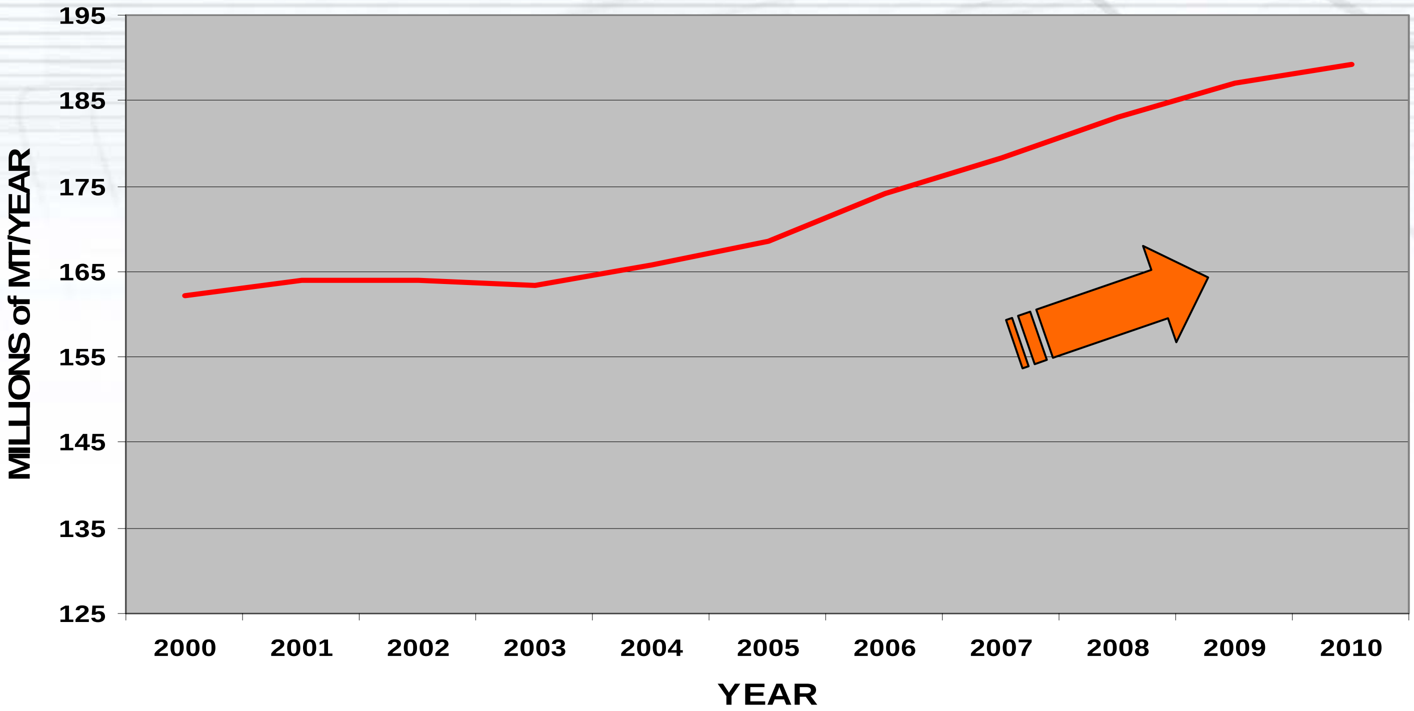
Ammonia Market Summary (Cont'd)



- 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 NH_3 via electrolysis will consume about:
  - 80,000-100,000 MW of electric power @ 3.5 kWh/Nm^3 of H_2
  - Ammonia equivalent to 60% of world capacity

- Ammonia is classified as a toxic chemical

- Ammonia Handling
  - Distribution
  - Storage
  - Transfer to vehicle tank

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THANK YOU