Ammonia

Dr. Mubarak

Topics to be Covered

- **Ammonia usages and properties**
- **Ammonia Supply & Demand**
- **History of Ammonia Manufacture**
- **Ammonia Plant Market Trends**
- **Current Manufacturing Technology**
- **Ammonia from Renewable Energy**

Uses of Ammonia

1- Fertilizer

Production of:

- **Ammonium sulfate, $(NH_4)_2SO_4$**
- **Ammonium phosphate, $(NH_4)3PO_4$**
- **Ammonium nitrate, NH_4NO_3**
- **Urea**

Uses of Ammonia

2- Chemicals

Synthesis of:

- **Nitric acid, HNO_3, which is used in making explosives such as TNT.**
- **Sodium hydrogen carbonate (sodium bicarbonate), $NaHCO_3$**
- **Sodium carbonate, Na_2CO_3**
- **Hydrogen cyanide (hydrocyanic acid), HCN**
- **Hydrazine, N_2H_4 (used in rocket propulsion systems)**

3- Explosives

Ammonium nitrate, NH_4NO_3

4- Fibers & Plastics

Nylon, $-[(CH_2)_4-CO-NH-(CH_2)_6-NH-CO]-$,and other polyamides.

5- Refrigeration

Used for making ice, large scale refrigeration plants, air-conditioning units in buildings and plants.

6- Pulp & Paper

Ammonium hydrogen sulfite, NH_4HSO_3, enables some hardwoods to be used

7- Pharmaceuticals

Used in the manufacture of drugs such as sulfonamide which inhibit the growth and multiplication of bacteria.

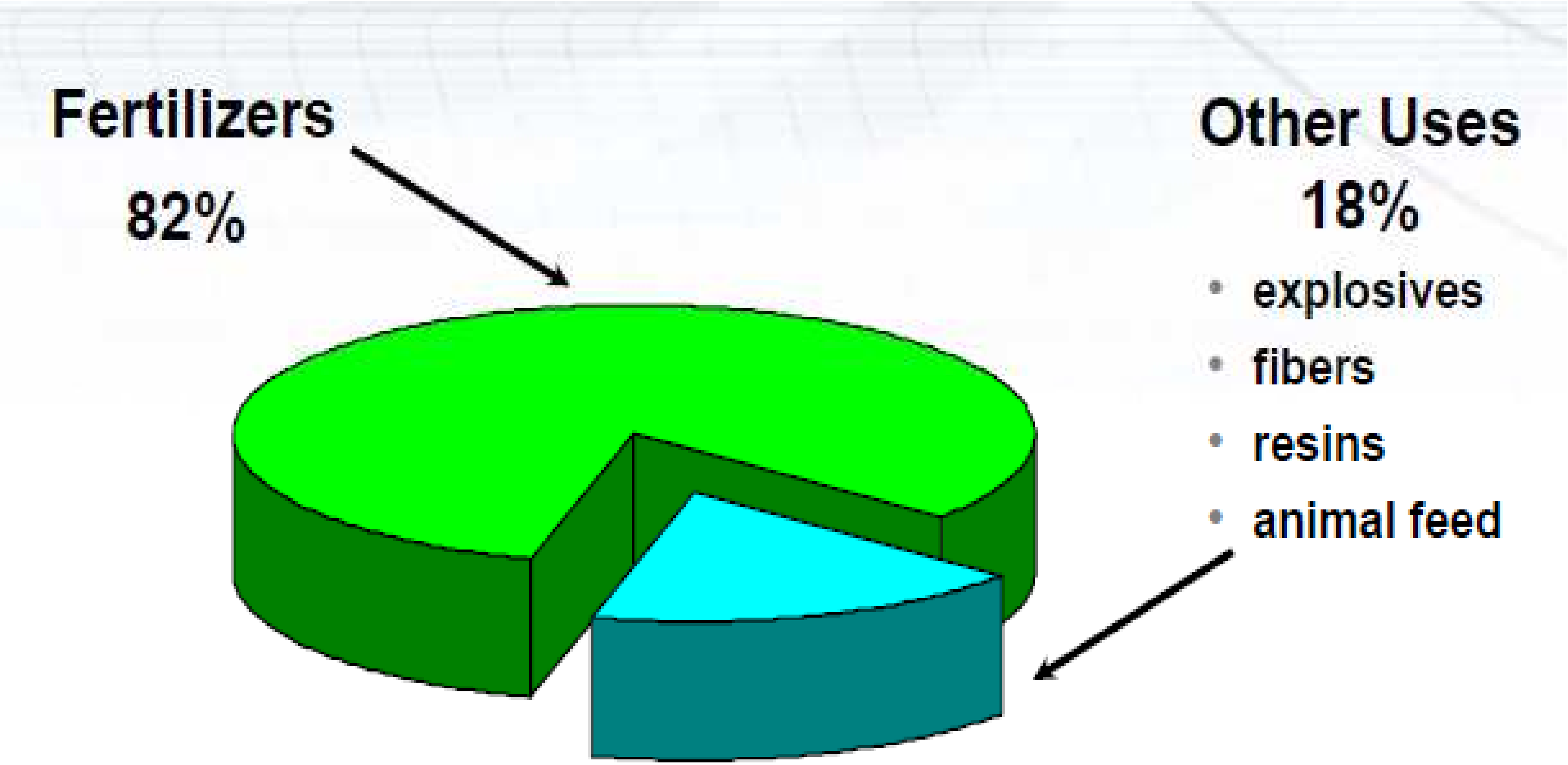
8- Mining & Metallurgy

Used in nitriding (bright annealing) steel, also used in zinc and nickel extraction

9- Cleaning

Ammonia in solution is used as a cleaning agent such as in 'cloudy ammonia‘.

Ammonia Uses



- explosives
- fibers
- resins
- animal feed

Ammonia Properties

1- Identification

Name: Ammonia

Commonly used synonyms: Liquid Ammonia

Molecular formula: NH_3

2. Hazards to the Environment and Man

To the environment

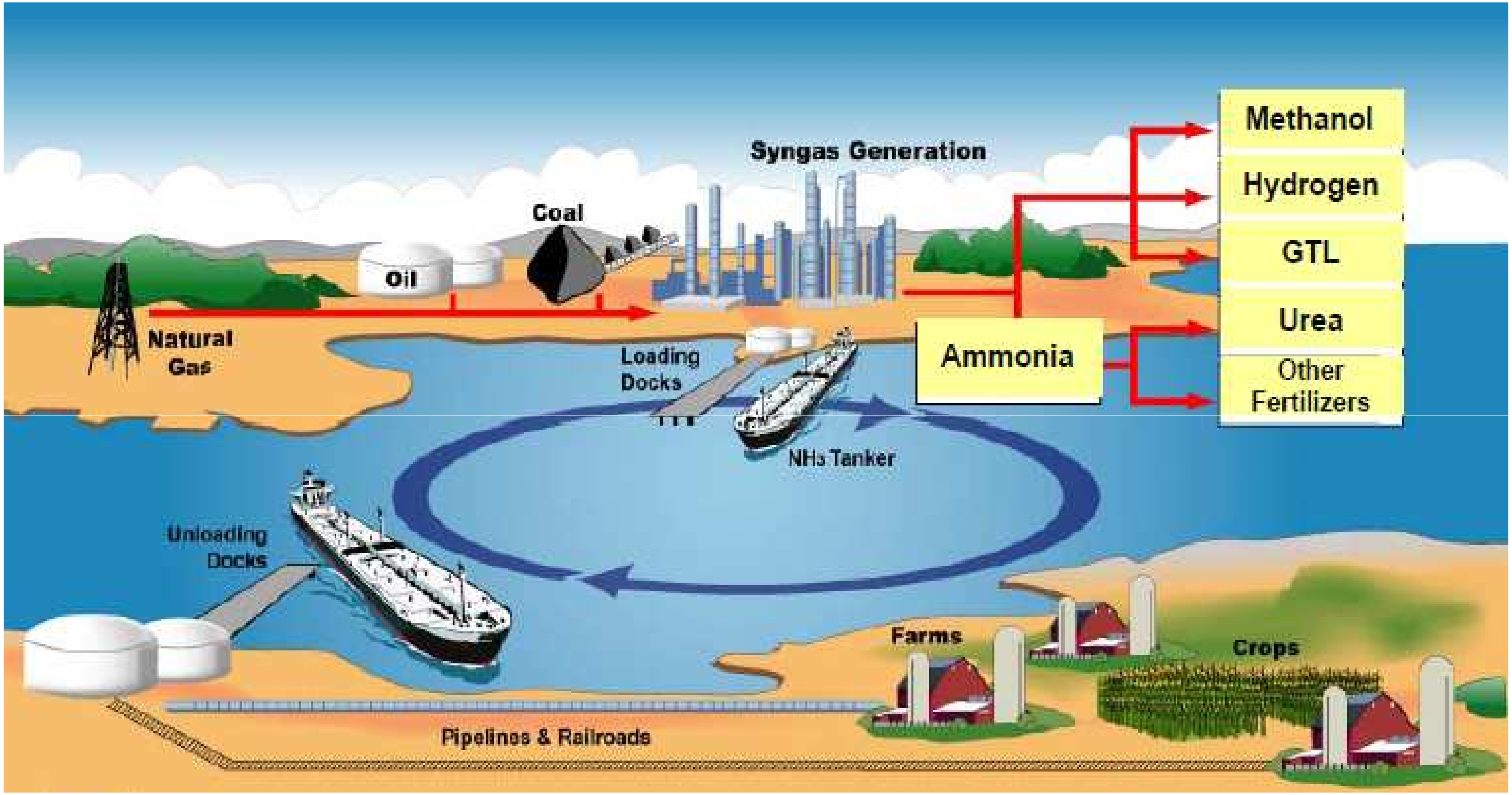
Ammonia is toxic to aquatic life

To man

- **Ammonia is toxic by inhalation and pulmonary edema lung may occur up to 48 hours after severe exposure and could be fatal.**
- **Vapors cause irritation and watering of eyes and in the presence of moisture, irritation of the skin.**
- **Liquid ammonia splashes may produce severe burns to the skin and permanent damage to the eyes.**
- **In enclosed spaces (eg vessels, closed workshops) ammonia vapor may be flammable/explosive.**

3- Physical and Chemical Properties

- Appearance: Colorless liquefied gas.
- Odor: Pungent, suffocating.
- pH water solution: (1%) 11.7
- Melting point (triple point): -77.7°C
- Boiling point: -33.4°C at 101.3 kPa
- Explosive limits: 16-27% NH_3 by vol. in air at 0°C
- Auto-ignition temperature: 651°C
- Vapor pressure: 1013kPa at 25°C
- Relative vapor density: 0.6 (air =1)
- Solubility in water: 529g/l at 20 °C
- Liquid density: 0.6386g/cm^3(at 0°C, 101.3kPa)
- Gas density: 0.7714g/l (at 0°C, 101.3kPa)


Syngas Generation
Coal
Oil
Natural Gas
Loading Docks
Ammonia
Methanol
Hydrogen
GTL
Urea
Other Fertilizers
NH3 Tanker
Unloading Docks
Farms
Crops
Pipelines & Railroads

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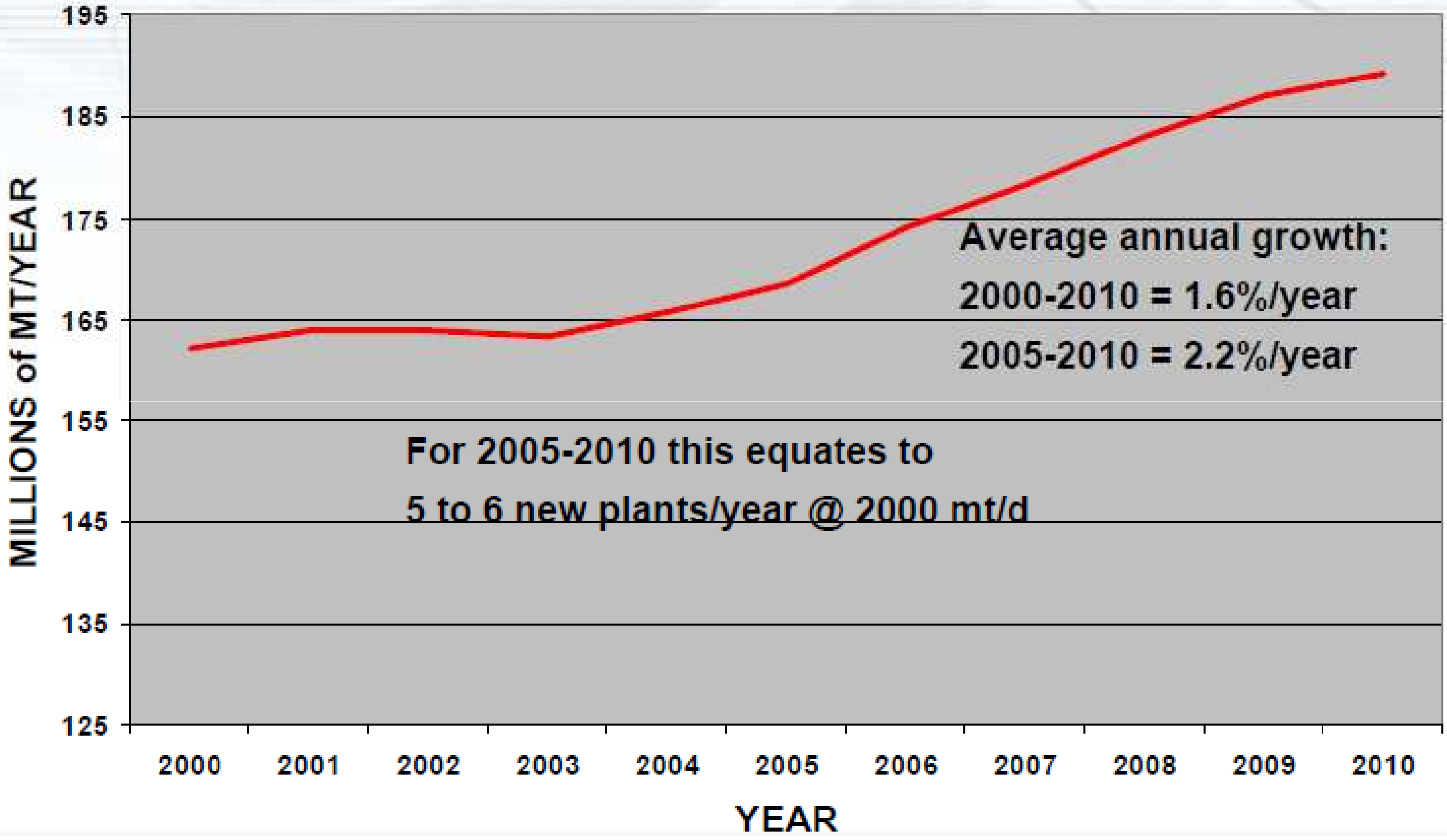
World Ammonia Capacity



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

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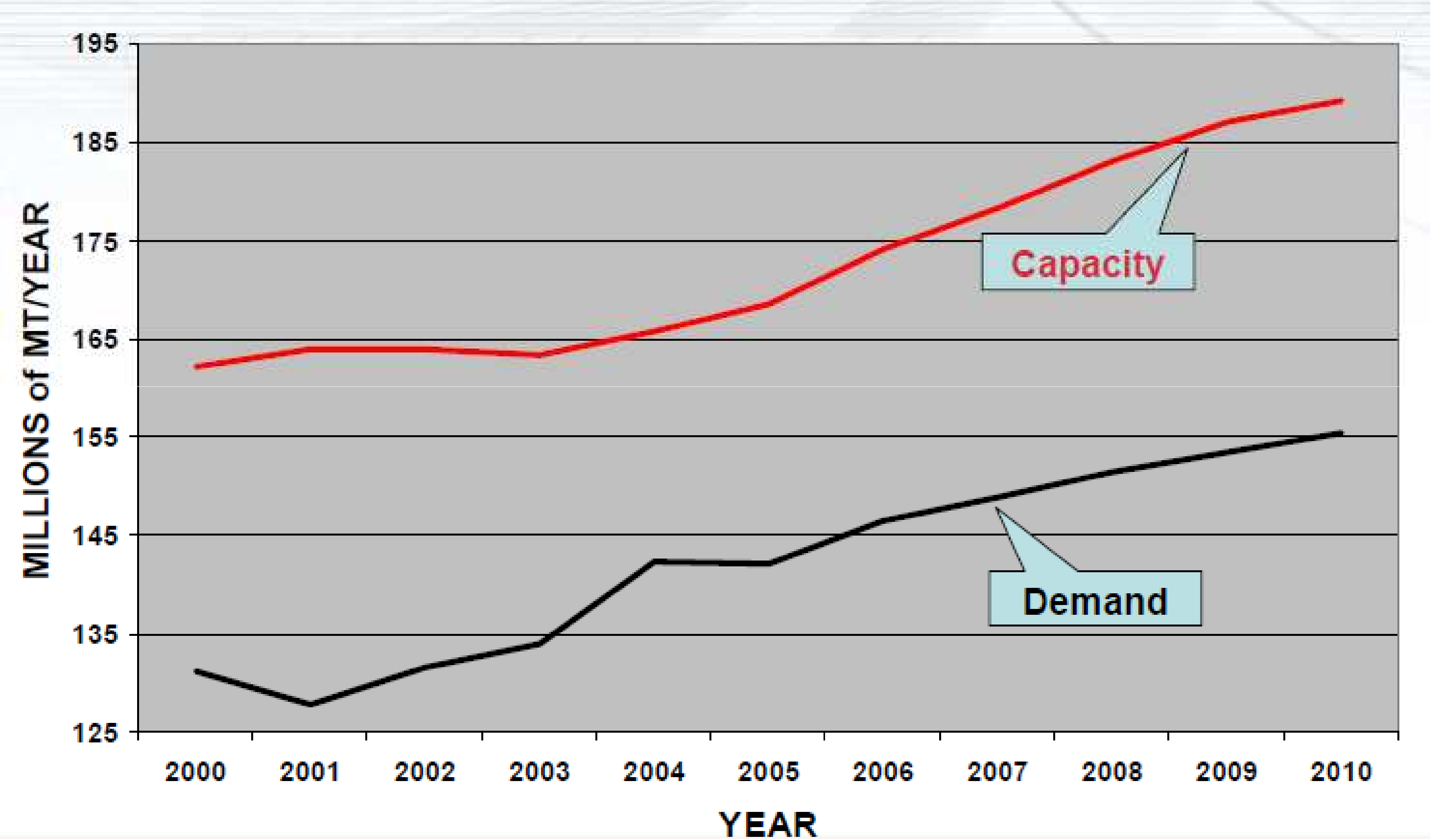
World Ammonia Capacity and Demand



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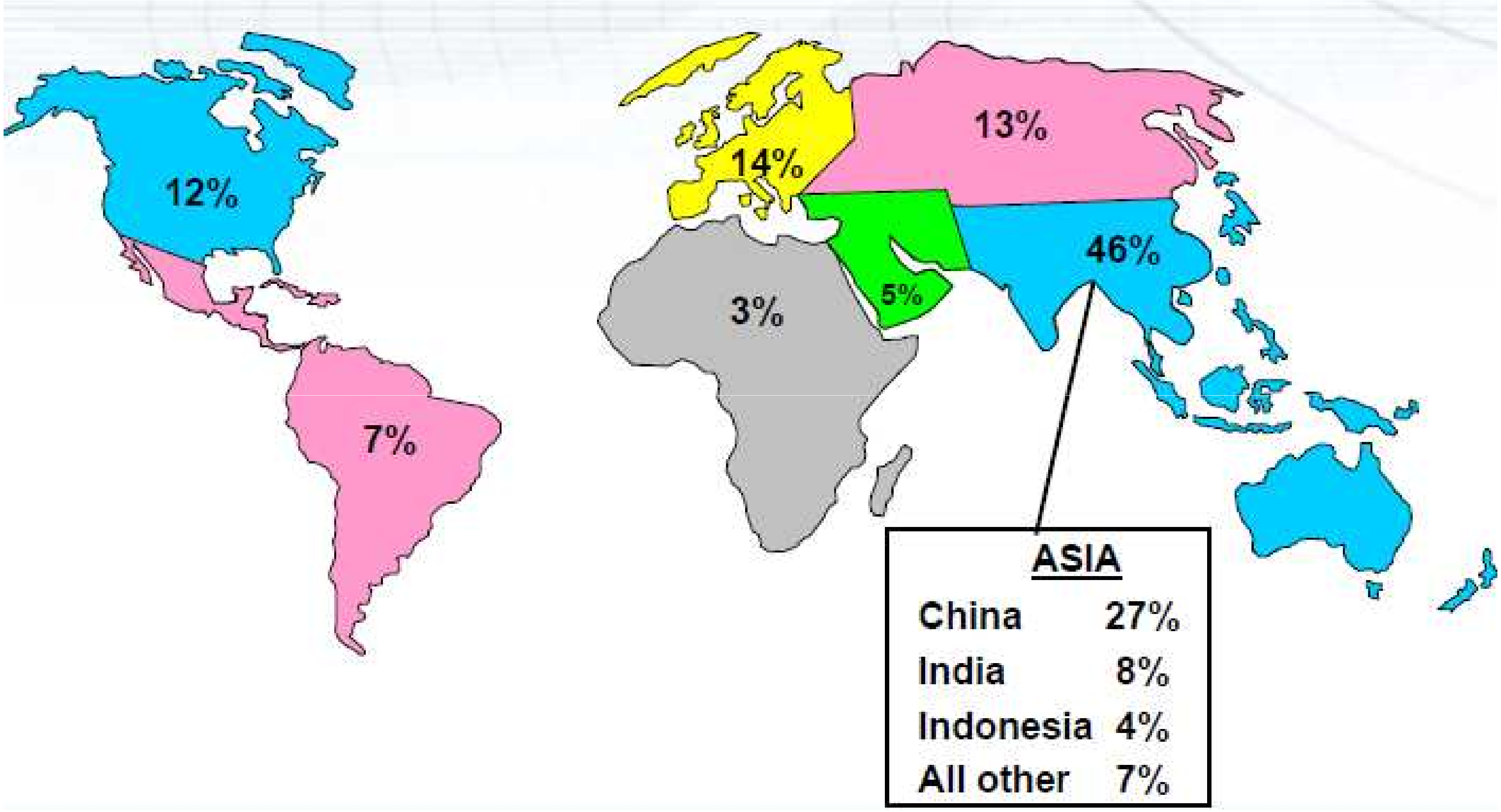
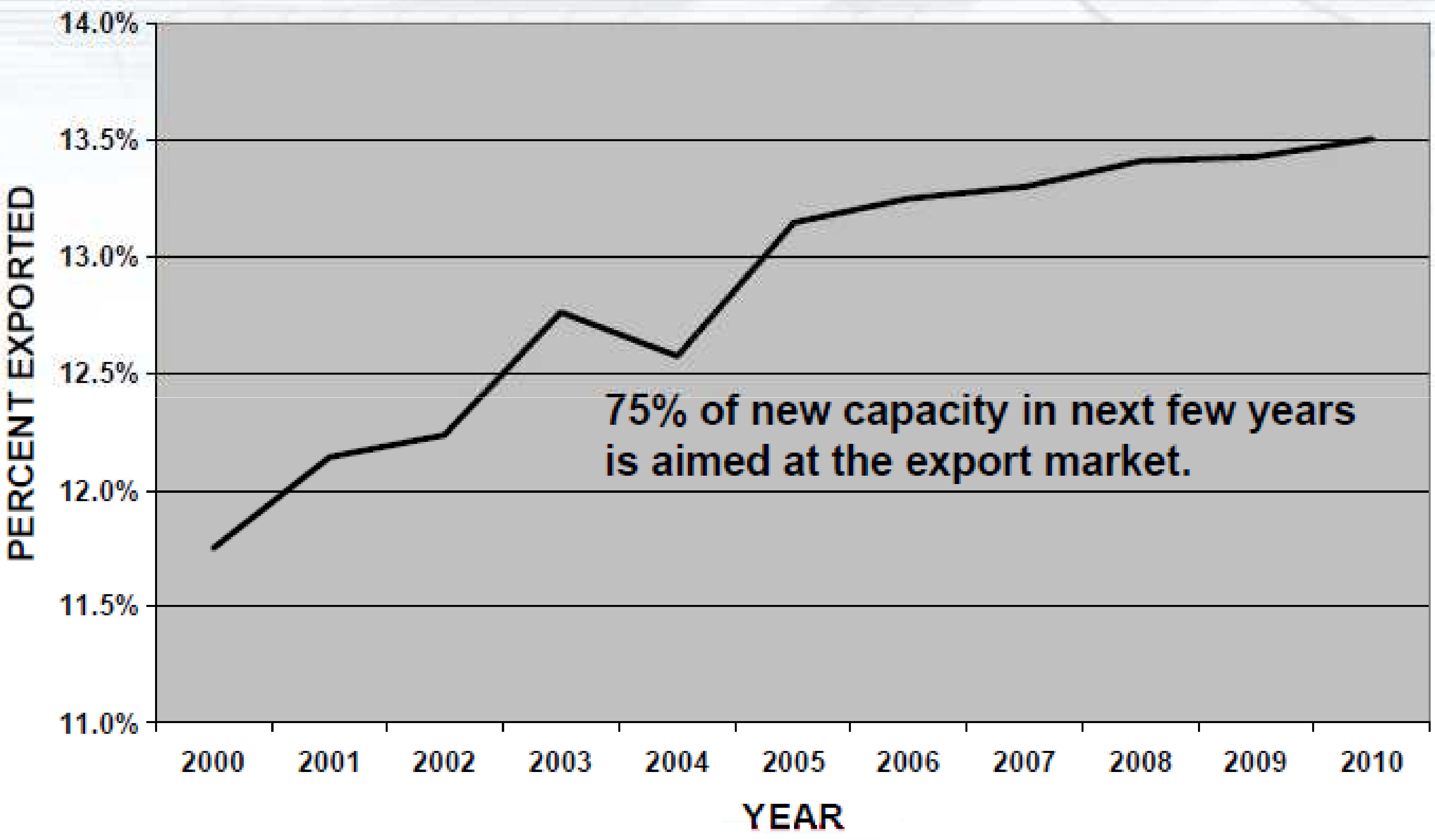
Ammonia Plant Capacity by Region



ASIA	
China	27%
India	8%
Indonesia	4%
All other	7%

Trends in World Ammonia Exports



75% of new capacity in next few years is aimed at the export market.

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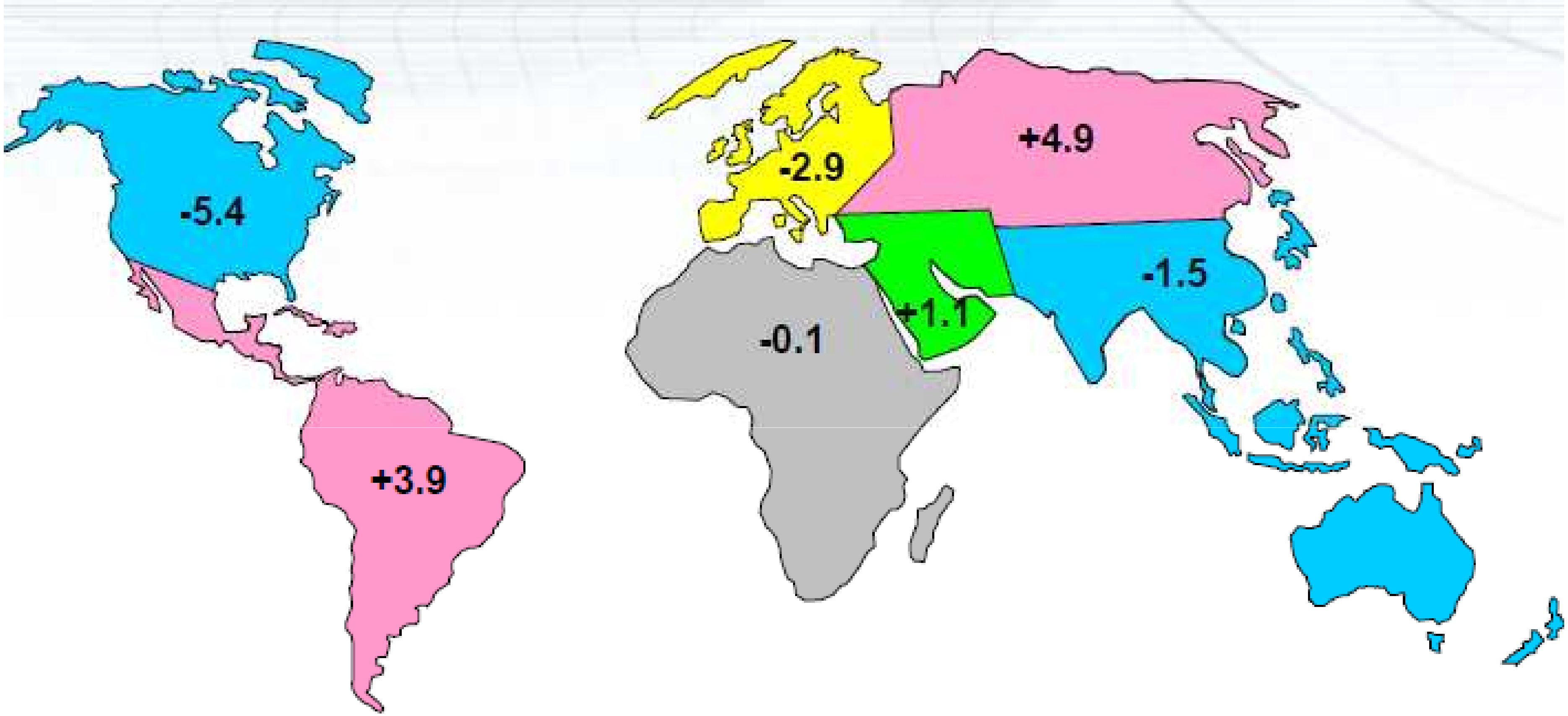
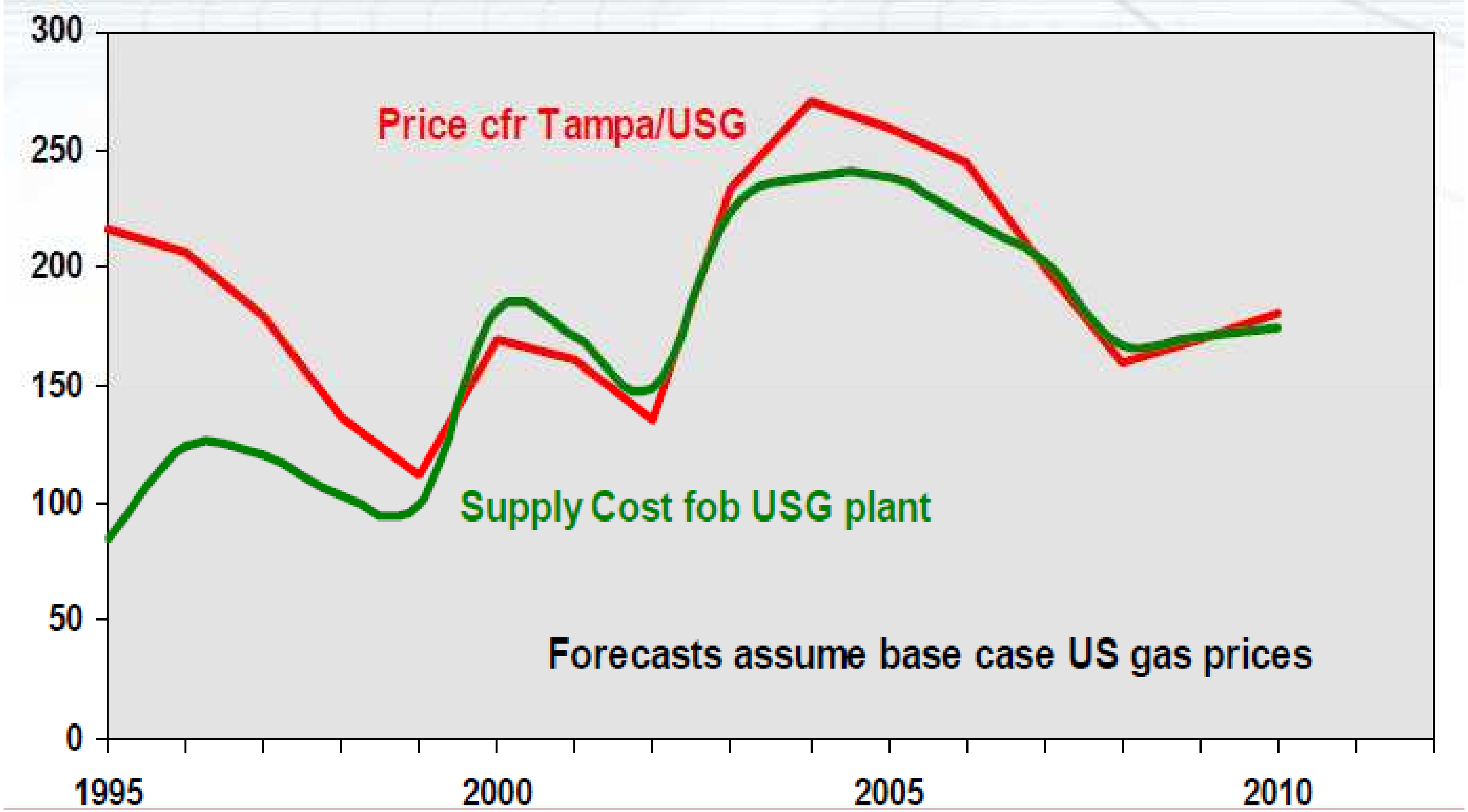
Net World Ammonia Trade in MT/Year



Total trade in 2004 = 17.9 mt (Fertecon)

Net trade in 2004 = 9.9 mt (Estimate)

Predicted US Golf Coast NH_3 Prices



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

- **Discovered by Robert Boyle in 1671.**

$$\mathbf{Fe + H_2SO_4 \rightleftharpoons FeSO_4 + H_2}$$

- **Recognized as an element in 1766 by Henry Cavendish.**
- **Named by Antoine Lavoisier in 1783 after he discovered its ability to generate water.**

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O}$$

History of Hydrogen Production

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

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

- **In early 20th century, coal was gasified with either air or oxygen to produce H_2 + CO mixtures for chemical synthesis.**
- **First steam-methane reformer on-line in 1931**

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

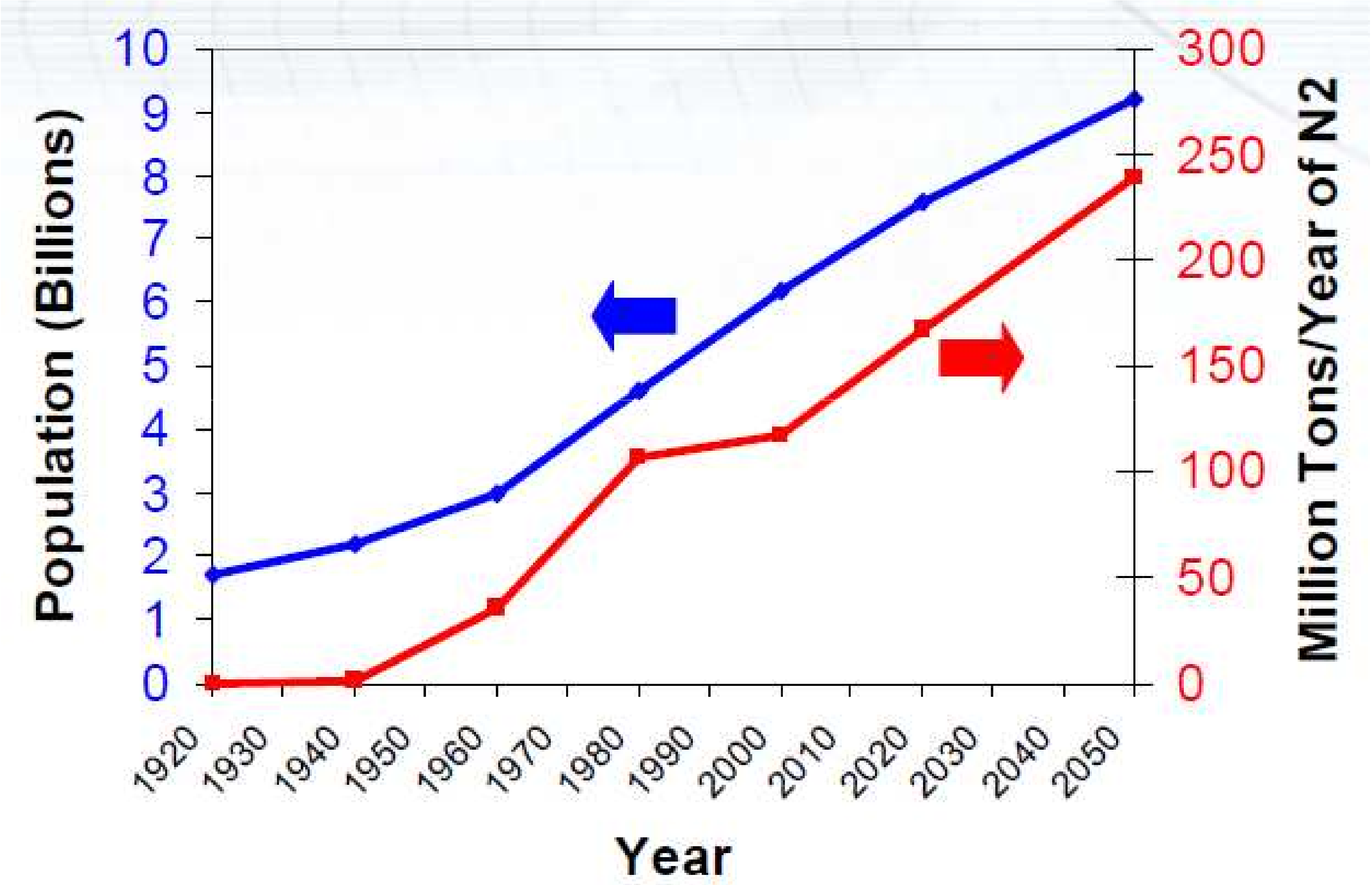
Hydrogen Sources for Making Ammonia

Process	Reaction	Re. Energy Consumption
Water electrolysis	$2H_2O \longrightarrow 2H_2+O_2$	300%
Coal gasification	$C+2H_2O \longrightarrow 2H_2+CO_2$	170%
Heavy fuel oil	$CH+2H_2O \longrightarrow 2.5H_2+CO_2$	135%
Naphtha reforming	$CH_2+2H_2 \longrightarrow 3H_2+CO_2$	104%
Nat. gas reforming	$CH_4+2H_2O \longrightarrow 4H_2+CO_2$	100%

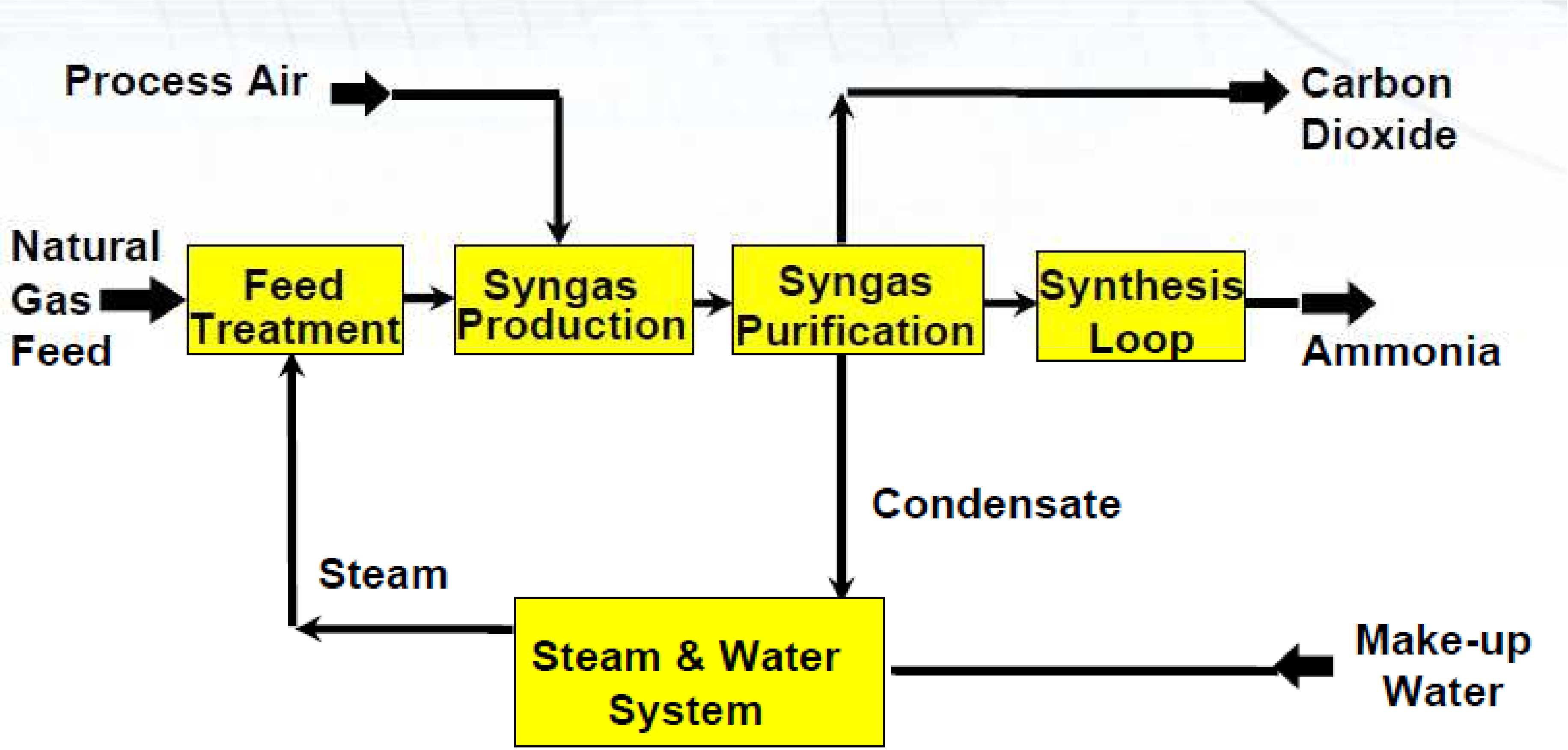
History of Ammonia Manufacture

	Year
Catalyst program by Haber & BASF	1908
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 450000 mt/d	2005

World Population & NH_3 Production



Sections in an Ammonia Plant



Description of production processes

- **At the beginning of the 20th century there was a shortage of naturally occurring, nitrogen-rich fertilizers, which prompted the German Chemist *Fritz Haber*, and others, to look for ways of combining the nitrogen in the air with hydrogen to form ammonia.**
- **This process was also of interest to the German chemical industry as Germany was preparing for World War I and nitrogen compounds were needed for explosives.**

- **The hydrogen for the ammonia synthesis was made by the water-gas process (a Carl Bosch invention) which involves blowing steam through a bed of red hot coke resulting in the separation of hydrogen from oxygen.**
- **The nitrogen was obtained by distillation of liquid air, then by cooling and compressing air.**
- **These days, the hydrogen is produced by reforming light petroleum fractions or natural gas (methane, CH_4) by adding steam:**

$$CH_4(g) + H_2O(g) \xrightarrow[700^oC]{\text{Ni catalyst}} CO(g) + 3H_2(g)$$

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- Enough steam is used to react with about 45% of the methane (CH_4) in the presence of Ni catalyst, the rest of the methane is reacted with air:

$$2CH_{4g} + O_{2g} + 4N_{2g} \longrightarrow 2CO_g + 4H_{2g} + 4N_{2g}$$

- All the carbon monoxide (CO) in the mixture is oxidized to CO_2 using steam and an iron oxide catalyst:

$$CO_g + H_2O_g \longrightarrow H_{2g} + CO_{2g}$$

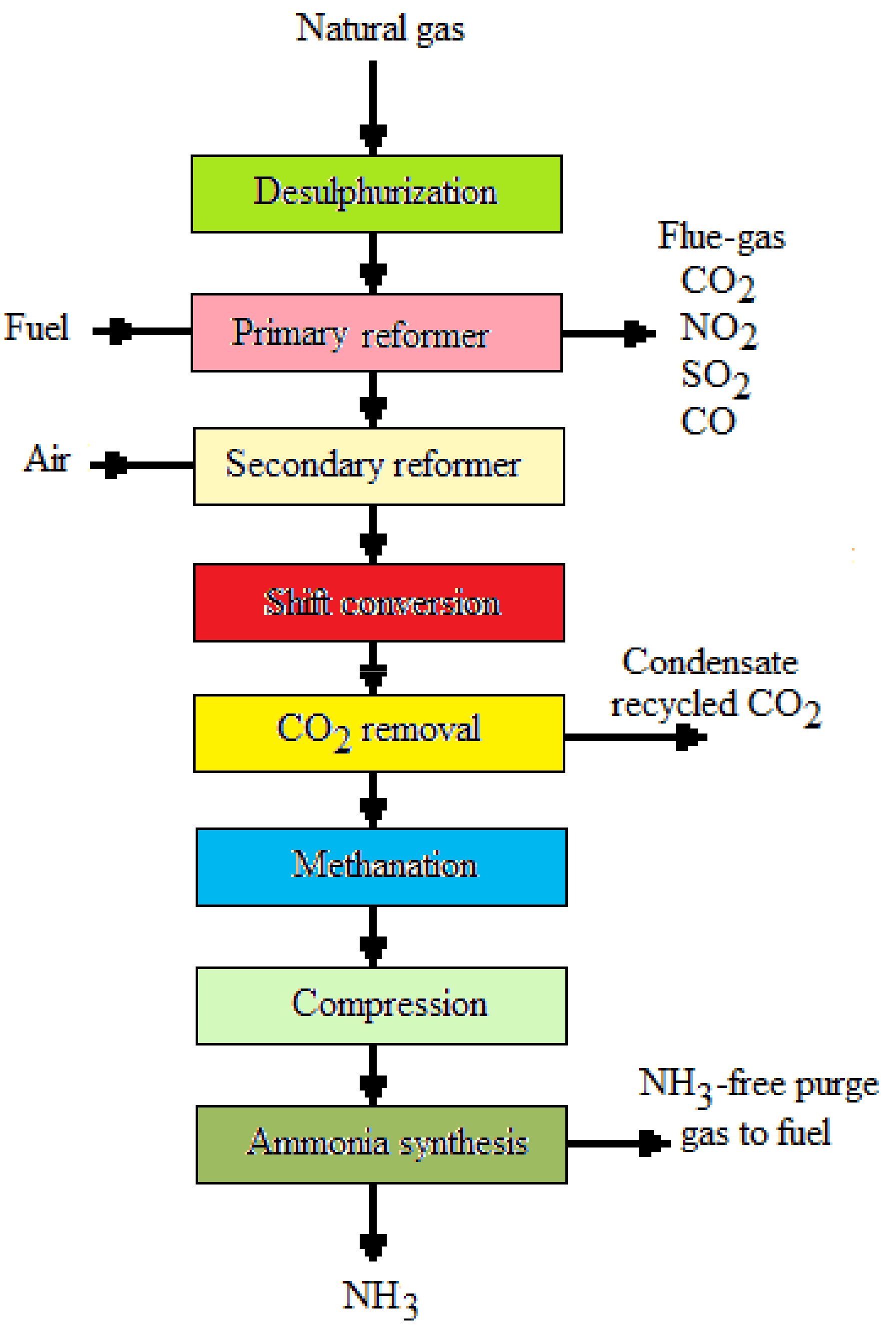
- The carbon dioxide (CO_2) is removed using a suitable base so that only the nitrogen gas (N_2) and hydrogen gas (H_2) remain and are used in the production of ammonia (NH_3).

1- Production Processes in Operation in Europe

- Two main types of production process for ammonia synthesis gas are currently in operation in Europe:-

1. Steam reforming of natural gas or other light hydrocarbons (Natural Gas Liquids, Liquefied Petroleum Gas, Naphtha).
2. Partial oxidation of heavy fuel oil or vacuum residue.

- Coal gasification and water electrolysis are no longer in use in the European ammonia industry.
- The ammonia synthesis process is principally independent of the type of synthesis gas production process, but synthesis gas quality influences the loop design and operating conditions.
- A block diagram of the conventional steam reforming process is shown in the Figure.
- About 85% of world ammonia production is based on steam reforming concepts.


Natural gas
Desulphurization
Fuel
Primary reformer
Flue-gas
CO_2
NO_2
SO_2
CO
Air
Secondary reformer
Shift conversion
Condensate
recycled CO_2
CO_2 removal
Methanation
Compression
NH_3-free purge
gas to fuel
Ammonia synthesis
NH_3

2- BAT Production Processes

- No single process can be identified as BAT for the production of ammonia.
- The characteristics of BAT processes based on available feedstocks are described.
- Natural gas reforming with steam and air is the simplest and most efficient way of ammonia synthesis gas production.
- Comparing natural gas reforming, heavy oil and coal gasification gives the following approximate relative consumption figures:

	Natural Gas	Heavy Oil	Coal
Energy consumption	1.0	1.3	1.7
Investment cost	1.0	1.4	2.4
Production cost	1.0	1.2	1.7

- **Based on the known resources of raw materials, it is likely that natural gas will dominate as the feedstock for ammonia for the next 50 years at least.**
- **In the very long term, 50-200 years, one might expect coal to take over, based on world reserves and consumption rate.**
- **Heavy oil may be attractive under special environmental concerns, when natural gas is not available and the partial oxidation process could solve a waste problem (heavy residues, plastics recycle).**

Conventional steam reforming

Overall conversion

- The theoretical process conversions, based on methane feedstock, are given in the following approximate formulae:-

  $0.88CH_4+1.26Air+1.24H_2O \longrightarrow 0.88CO_2+N_2+3H_2$

  $N_2+3H_2 \longrightarrow 2NH_3$
- The synthesis gas production and purification normally take place at 25-35 bar pressure.
- The ammonia synthesis pressure is usually in the range 100-250 bar.

Feedstock desulphurization

- **Most of the catalysts used in the process are sensitive to sulfur and sulfur compounds.**
- **The feedstock normally contains traces of sulfur compounds.**
- **The feed-gas is pre-heated to 350-400°C, usually in the primary reformer convection section, and then treated in a desulphurization vessel, where the sulfur compounds are hydrogenated to H_2S, typically using a cobalt molybdenum catalyst, and then adsorbed on pelletized zinc oxide:-**

Feedstock desulphurization

$$R\text{-}SH + H_2 \rightarrow H_2S + RH$$

$$H_2S + ZnO \rightarrow ZnS + H_2O$$

- In this way, the sulfur is removed to less than 0.1 ppm S in the gas feed.
- The zinc sulfide remains in the adsorption bed.
- The hydrogen for the reaction is usually recycled from the synthesis section.

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

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

Primary reforming

- The gas from the desulphuriszer is mixed with process steam, usually coming from an extraction turbine.
- The steam/gas mixture is then heated further to 500-600°C in the convection section before entering the primary reformer.
- In some new or revamped plants the preheated steam/gas mixture is passed through an adiabatic pre-reformer and reheated in the convection section, before entering the primary reformer.

- **Also, in some plants, part of the process steam is supplied by feed-gas saturation.**
- **The amount of process steam is given by the process steam to carbon molar ratio (S/C-ratio), which should be around 3.0 for the BAT reforming processes.**
- **The optimum ratio depends on several factors, such as feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and the plant steam balance.**
- **In new plants the optimum S/C-ratio may be lower than 3.0.**

- The primary reformer consists of a large number of high-nickel chromium alloy tubes filled with nickel-containing reforming catalyst.
- The overall reaction is highly endothermic and additional heat is required to raise the temperature to 780-830°C at the reformer outlet.
- The composition of the gas leaving the primary reformer is given by close approach to the following chemical equilibria:-

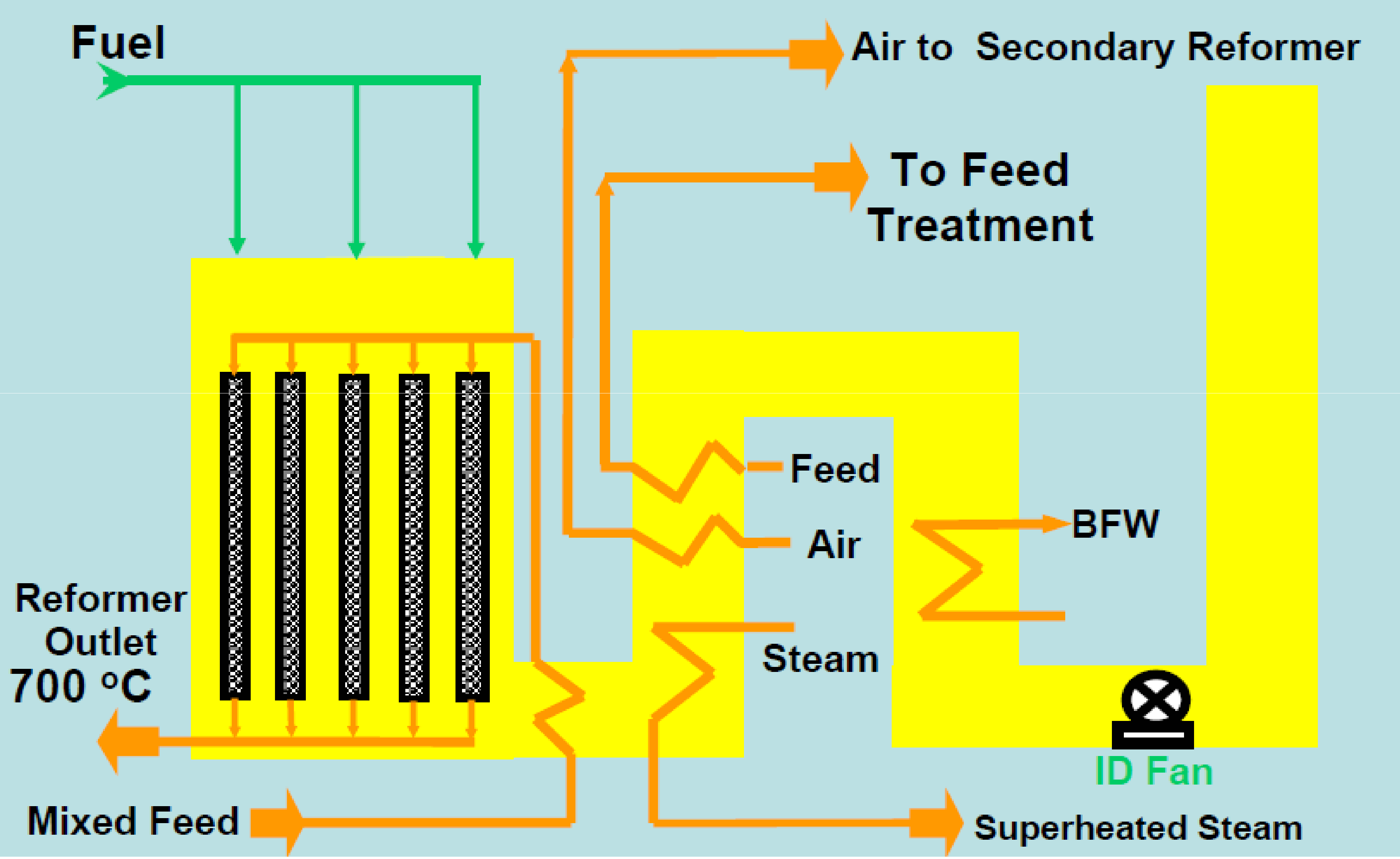
$CH_4 + H_20 \Longleftrightarrow CO + 3H_2 \qquad \Delta H^o_{298} = 206\ kJ.mol^{-1}$

$C0 + H_20 \Longleftrightarrow CO_2 + H_2 \qquad \Delta H^o_{298} = -41\ kJ.mol^{-1}$

- **The heat for the primary reforming process is supplied by burning natural gas or other gaseous fuel, in the burners of a radiant box containing the tubes.**
- **The flue-gas leaving the radiant box has temperatures in excess of 900 °C, after supplying the necessary high level heat to the reforming process.**
- **Thus only about 50-60% of the heat value is directly used in the process itself.**

- **The heat content (waste heat) of the flue-gas is used in the reformer convection section, for various process and steam system duties.**
- **The fuel energy requirement in the conventional reforming process is 40-50% of the process feed-gas energy.**
- **The flue-gas leaving the convection section at 100-200°C is one of the main sources of emissions from the plant.**
- **These emissions are mainly CO_2, NO_x, with small amounts of SO_2 and CO.**

Primary Reforming



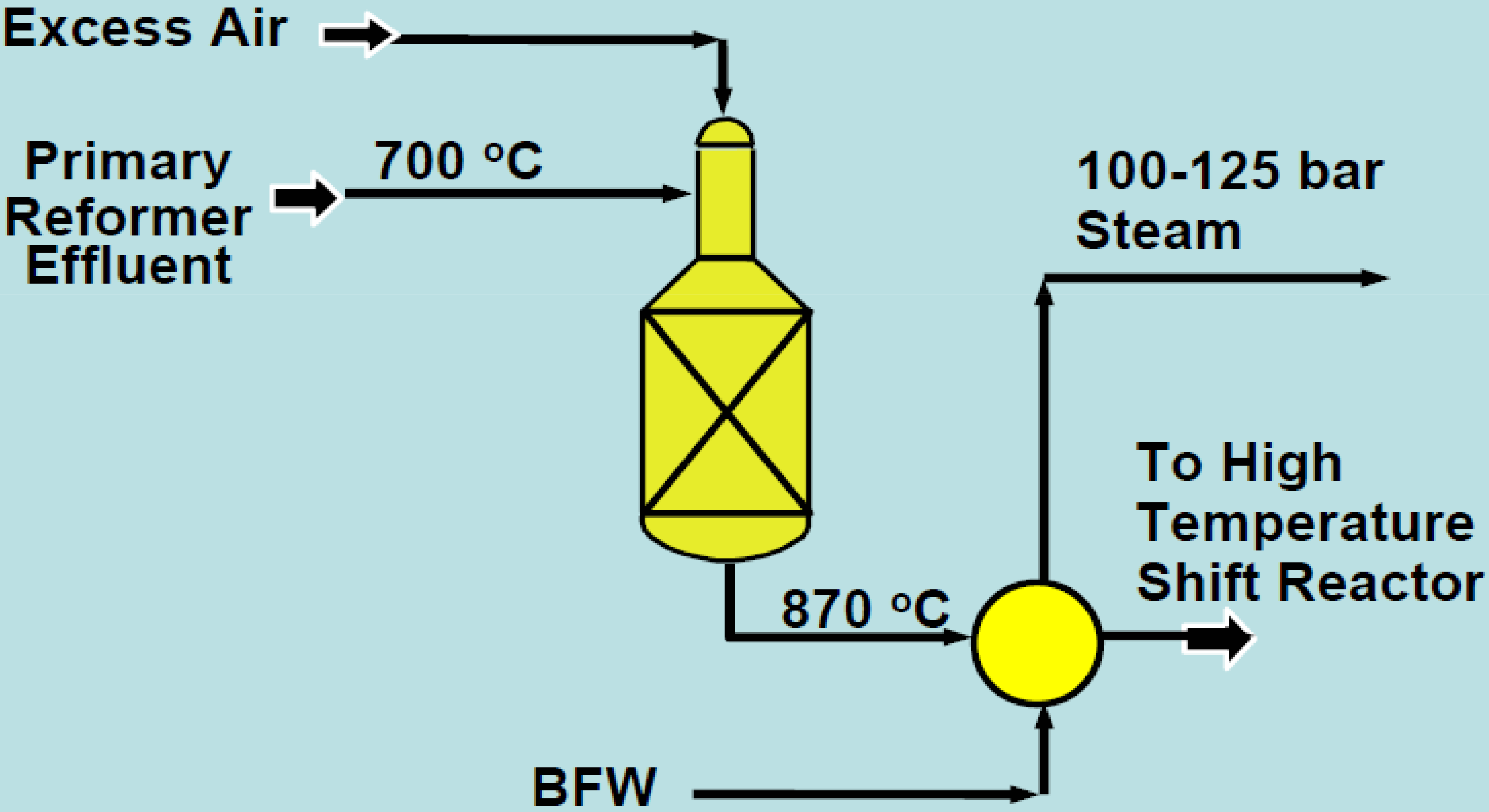
Secondary reforming

- Only 30-40% of the hydrocarbon feed is reformed in the primary reformer because of the chemical equilibria at the actual operating conditions.
- The temperature must be raised to increase the conversion.
- This is done in the secondary reformer by internal combustion of part of the gas with the process air, which also provides the nitrogen for the final synthesis gas.

- **In the conventional reforming process the degree of primary reforming is adjusted so that the air supplied to the secondary reformer meets both the heat balance and the stoichiometric synthesis gas requirement.**
- **The process air is compressed to the reforming pressure and heated further in the primary reformer convection section to around 600°C.**
- **The process gas is mixed with the air in a burner and then passed over a nickel-containing secondary reformer catalyst.**

- **The reformer outlet temperature is around 1,000°C, and up to 99% of the hydrocarbon feed (to the primary reformer) is converted, giving a residual methane content of 0.2-0.3% (dry gas base) in the process gas leaving the secondary reformer.**
- **The process gas is cooled to 350-400°C in a waste heat steam boiler or boiler/superheater downstream from the secondary reformer.**

Secondary Reforming



Excess Air

Primary Reformer Effluent

700 °C

100-125 bar Steam

To High Temperature Shift Reactor

870 °C

BFW

Shift conversion

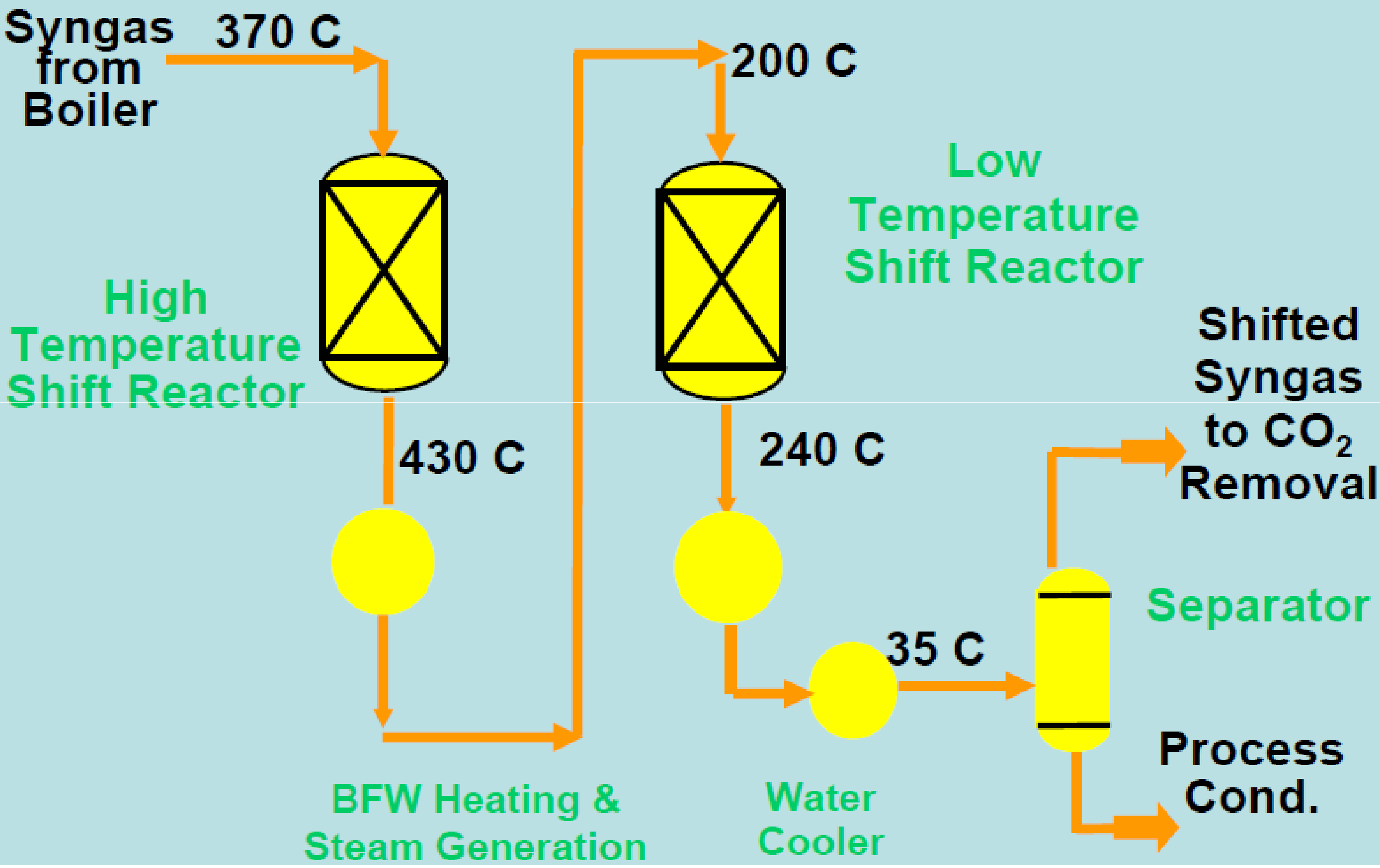
- The process gas from the secondary reformer contains 12-15% CO (dry gas base) and most of the CO is converted in the shift section according to the reaction:-

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H^o_{298} = -41\ kJ.mol^{-1}$$

- In the High Temperature Shift (HTS) conversion, the gas is passed through a bed of iron oxide/chromium oxide catalyst at around 400 °C, where the CO content is reduced to about 3% (dry gas base), limited by the shift equilibrium at the actual operating temperature.

- **There is a tendency to use copper containing catalyst for increased conversion.**
- **The gas from the HTS is cooled and passed through the Low Temperature Shift (LTS) converter.**
- **This LTS converter is filled with a copper oxide/zinc oxide-based catalyst and operates at about 200-220°C.**
- **The residual CO content in the converted gas is about 0.2-0.4% (dry gas base).**
- **A low residual CO content is important for the efficiency of the process.**

Shift Conversion



Syngas from Boiler

370 C

High Temperature Shift Reactor

430 C

BFW Heating & Steam Generation

200 C

Low Temperature Shift Reactor

240 C

Water Cooler

35 C

Separator

Shifted Syngas to CO_2 Removal

Process Cond.

CO_2 removal

- **The process gas from the low temperature shift converter contains mainly H_2, N_2, CO_2 and the excess process steam.**
- **The gas is cooled and most of the excess steam is condensed before it enters the CO_2 removal system.**
- **This condensate normally contains 1500 - 2000ppm of ammonia 800 - 1200ppm of methanol.**
- **Minor amounts of amines, formic acid and acetic acid could be present in the condensate.**

- **All these components should be stripped from the condensate and/or recycled in BAT processes.**
- **The heat released during cooling / condensation is used for:-**
  1. **The regeneration of the CO2scrubbing solution.**
  2. **Driving an absorption refrigeration unit.**
  3. **Boiler feed water preheat**

- **The amount of heat released depends on the process steam to carbon ratio.**

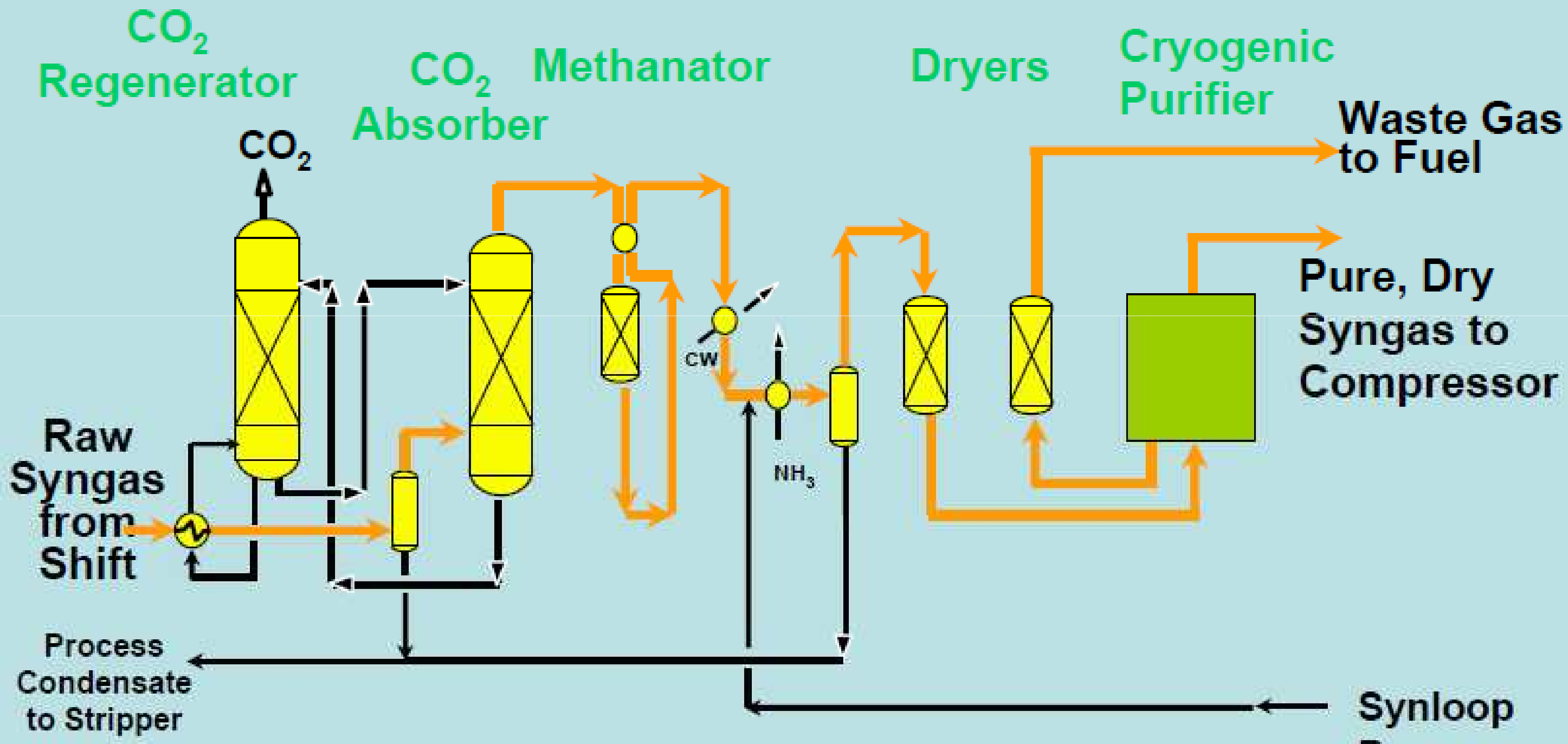
- **If all this low-level heat is used for CO_2 removal or absorption refrigeration, high-level heat has to be used for the feed water system.**
- **An energy-efficient process should therefore have a CO_2 removal system with a low heat demand.**
- **The CO_2 is removed in a chemical or a physical absorption process.**
- **The solvents used in chemical absorption processes are mainly aqueous amine solutions (Mono Ethanolamine (MEA), Activated Methyl DiEthanolamine (aMDEA) or hot potassium carbonate solutions.**

- Physical solvents are glycol dimethylethers (Selexol), propylene carbonate and others.
- The MEA process has a high regeneration energy consumption and is not regarded as a BAT process.
- For new ammonia plants the following CO_2 removal processes are currently regarded as BAT:-

1. aMDEA standard 2-stage process, or similar
2. Benfield process (HiPure, LoHeat), or similar
3. Selexol or similar physical absorption processes.

- **The typical range of heat consumption in the modern chemical absorption process is 30-60 MJ.kmol^{-1} CO_2.**
- **The physical absorption processes may be designed for zero heat consumption, but for comparison with the chemical processes, the mechanical energy requirements have also to be considered.**
- **Residual CO_2 contents are usually in the range 100-1000 ppm, dependent on the type and design of the removal unit.**
- **Contents down to about 50ppmv are achievable.**

Syngas Purification



CO_2 Removal System

1500 t/d plant in China

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Methanation

- The small amounts of CO and CO2, remaining in the synthesis gas, are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH4 in the methanator:-

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

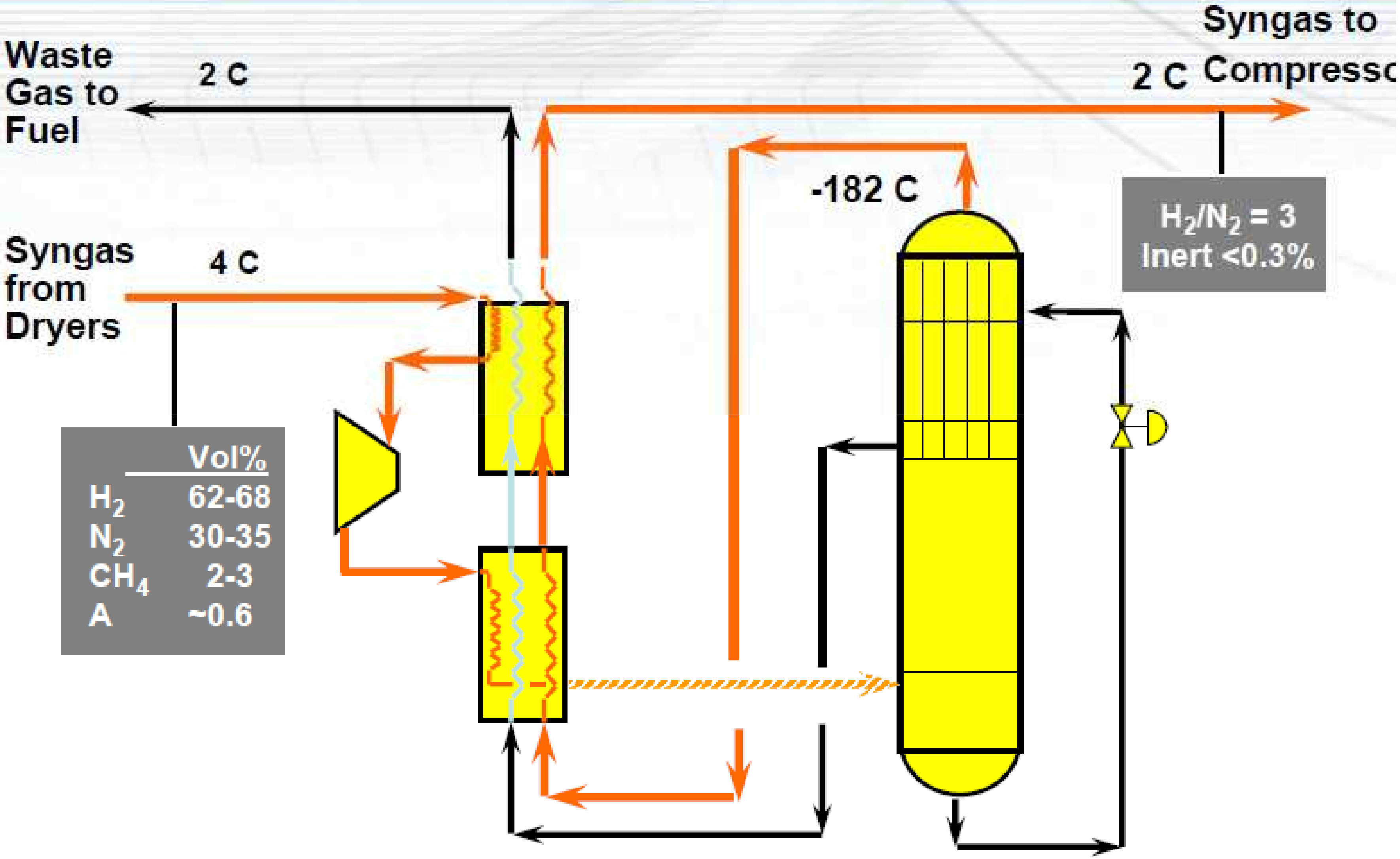
$$CO2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

- The reactions take place at around 300 °C in a reactor filled with a nickel containing catalyst.

- **Methane is an inert gas in the synthesis reaction, but the water must be removed before entering the converter.**
- **This is done firstly by cooling and condensation downstream of the methanator and finally by condensation/absorption in the product ammonia in the loop or in a make-up gas drying unit.**


Catalyst

KBR Cryogenic Purifier



Waste Gas to Fuel

2 C

Syngas to Compresso

2 C

-182 C

$H_2/N_2 = 3$
Inert <0.3%

Syngas from Dryers

4 C

	Vol%
H_2	62-68
N_2	30-35
CH_4	2-3
A	~0.6

Ammonia Converter

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Synthesis gas compression and ammonia synthesis

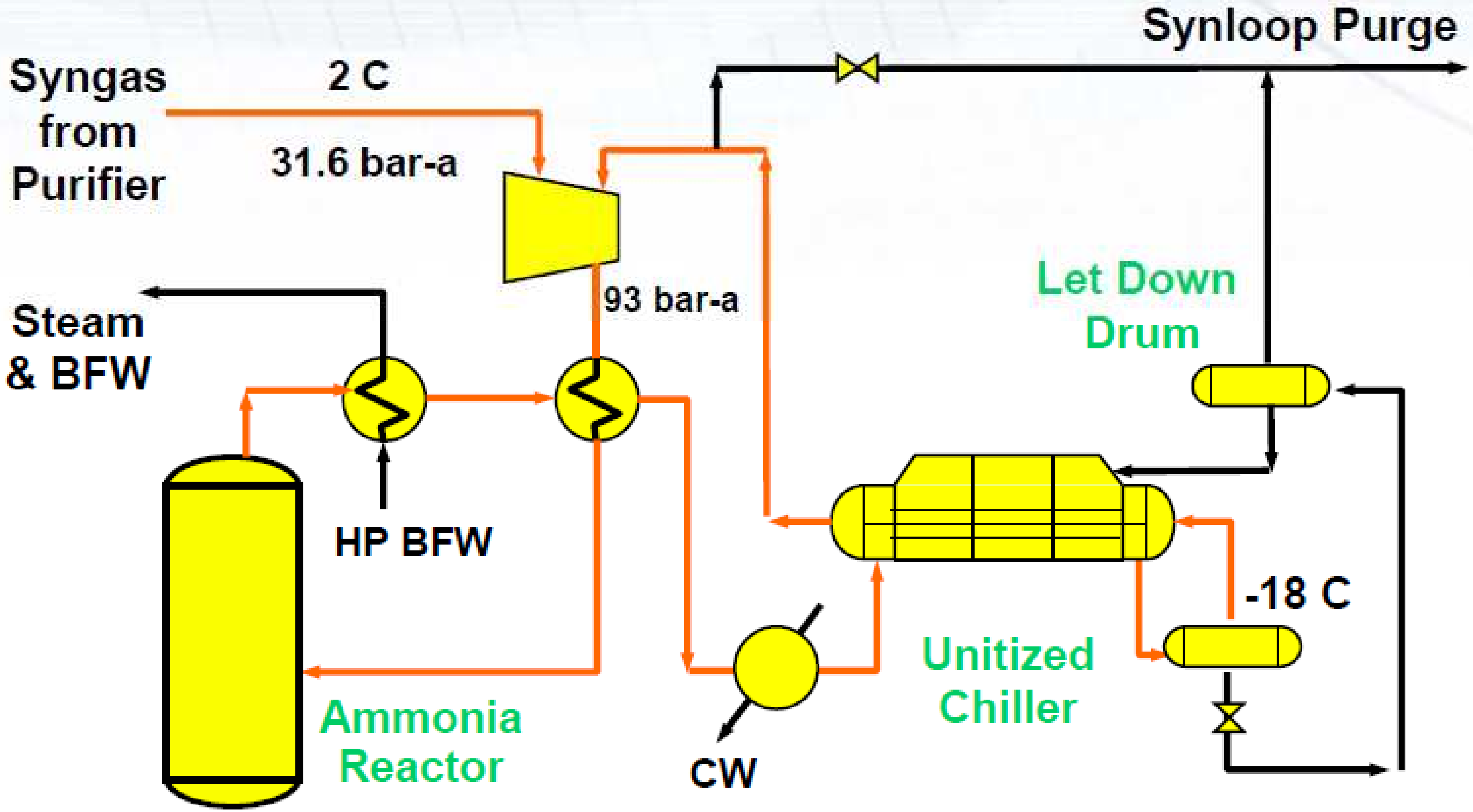
- Modern ammonia plants use centrifugal compressors for synthesis gas compression, usually driven by steam turbines, with the steam being produced in the ammonia plant.
- The refrigeration compressor, needed for condensation of product ammonia, is also usually driven by a steam turbine.
- The synthesis of ammonia takes place on an iron catalyst at pressures usually in the range 100 - 250 bar and T in the range 350 - 550 °C:-

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H^o_{298} = -46\ kJ.mol^{-1}\ NH_3$$

- **Only 20-30% is reacted per pass in the converter due to the unfavourable equilibrium conditions.**
- **The ammonia that is formed is separated from the recycle gas by cooling/condensation, and the reacted gas is substituted by the fresh make-up synthesis gas, thus maintaining the loop pressure.**
- **In addition, extensive heat exchange is required due to the exothermic reaction and the large temperature range in the loop.**

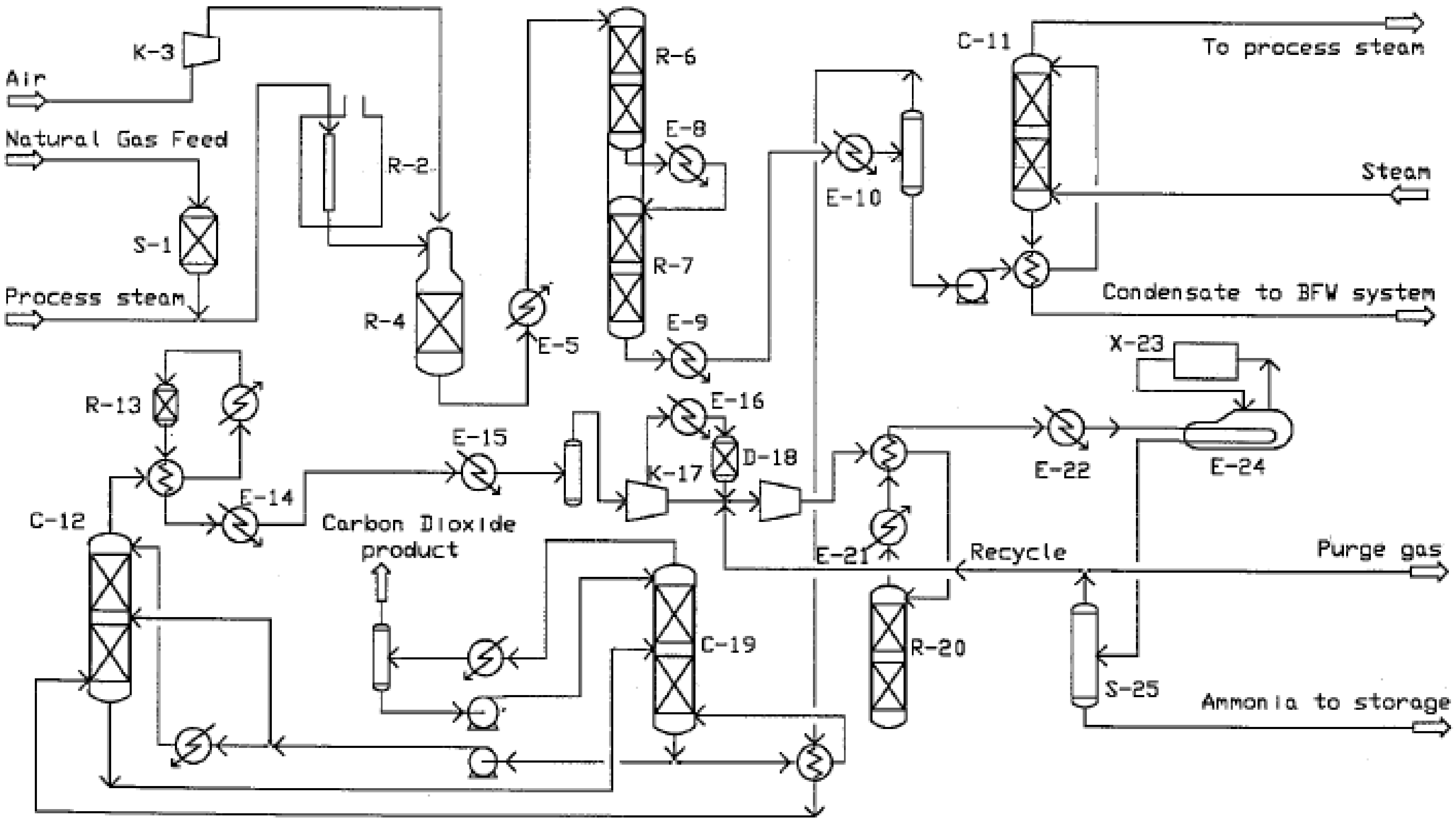
- **A newly developed ammonia synthesis catalyst containing ruthenium on a graphite support has a much higher activity per unit of volume and has the potential to increase conversion and lower operating pressures.**

Ammonia Synthesis Loop



Steam and power system

- Steam reforming ammonia plants have high-level surplus heat available for steam production in the reforming, shift conversion, and synthesis sections, and in the convection section of the primary reformer.
- Most of this waste heat is used for high pressure steam production for use in turbines for driving the main compressors and pumps and as process steam extracted from the turbine system.
- A modern steam reforming ammonia plant can be made energetically self-sufficient if necessary.



Legend:

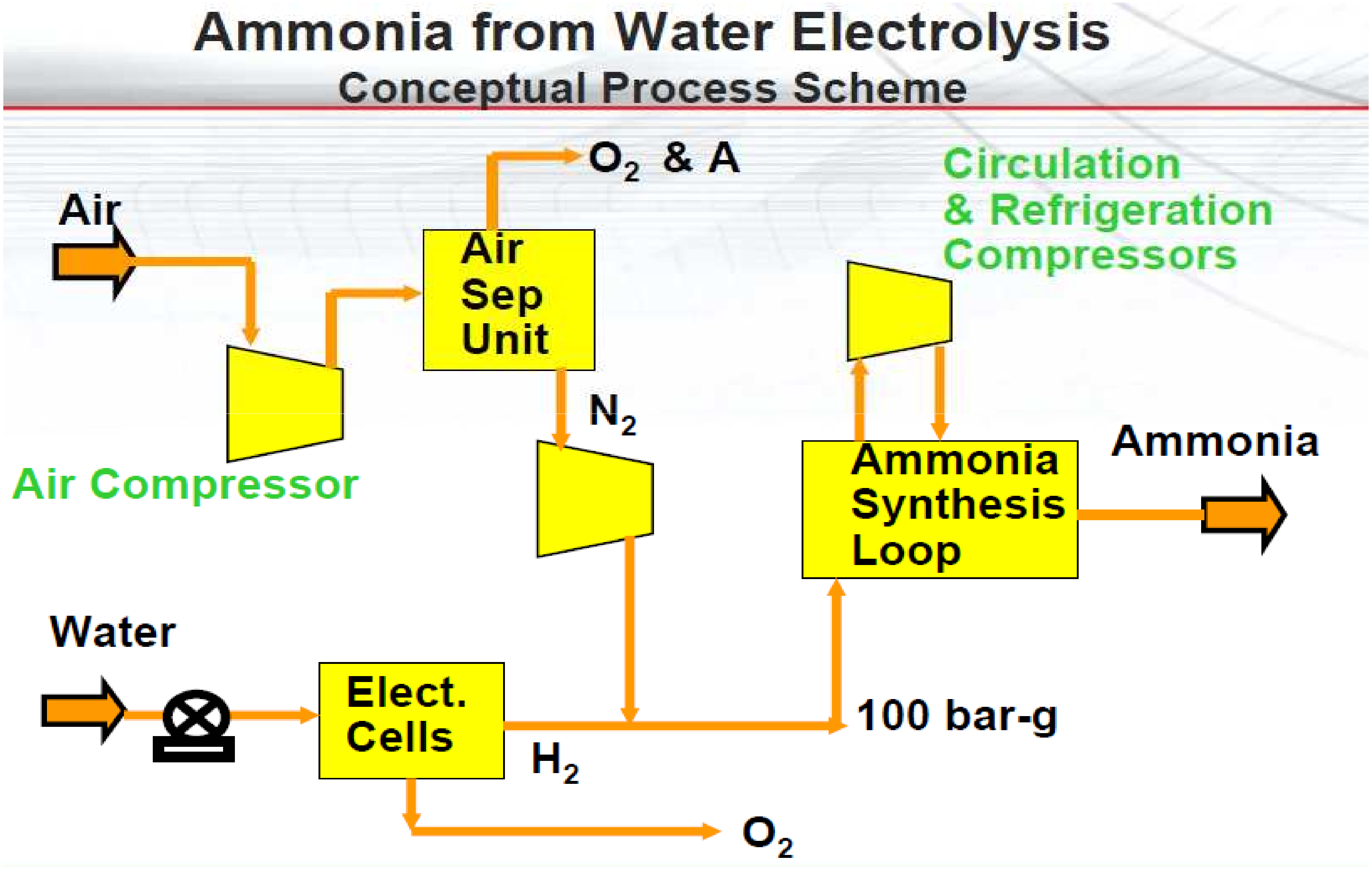
S-1 Sulfur removal
R-2 Primary reformer
K-3 Air compressor
R-4 Secondary reformer
E-5, E-7, E-8 Heat recovery

R-6 HT shift converter
R-7 LT shift converter
E-10 Cooler
C-11 Condensate stripper
C-12 CO2 absorber

R-13 Methanator
E-14, E-21 Heat recovery
E-15, E-22 Cooler
E-16 Syn-gas cooler
K-17 Syn-gas compressor

D-18 Dryer
C-19 CO2 stripper
R-20 Ammonia converter
X-23 NH3 refrigeration
E-24 Chiller
S-25 HP separator

Ammonia from Renewable Energy



Dr. Mubarak

BAT reforming processes for new plants and power system

- **The modern versions of the conventional steam reforming and excess air reforming processes will still be used for new plants for many years to come. Developments are expected to go in the following directions:-**

1. **Lowering the steam to carbon ratio**
2. **Shifting duty from primary to secondary reformer**
3. **Improved final purification**
4. **Improved synthesis loop efficiency**

1. **Improved power energy system**
2. **Low NO_x burners**
3. **Non iron based ammonia synthesis catalyst**