Ammonia Synthesis

About Me

Teaching Philosophy

- Teaching/Learning is a two-way exchange of knowledge and a close interaction between a teacher and a student
- How do we learn? An old proverb captures the essence of learning process - *I hear and I forget; I see and I remember; I do and I understand*.
- Though I am very much doubtful about my ability, **Ask question; Rationalize your answers.**

"Active inquiry, not passive absorption, is what engages students. It should pervade the curriculum"

Johnson, Spalding, Paden & Ziffen, 1989

On learning and securing good marks

- In this course, emphasis is placed on deeper understanding and learning more information about both Fertilizer and Pulp and paper technology.

- <u>Understanding of engineering concepts.</u>

- Assessment will be based on understanding process and depth of engineering concepts. (Memorizing power?)

Code of Conduct

- Turn off your cell phone when you enter the classroom
- Keep the internal discussions to a minimum
  - Background chattering noise is distracting for the instructor and eventually to classmates
  - If you have something interesting to share, share it with the whole class
- If you are sleepy, your bed may provide a better environment for rest than the classroom chair

What I expect of you

General Expectations

- Help each other understand the course material
- Ask question whenever something is not clear to you
- Perform all assigned reading on time
- Arrive on-time for class
- Be courteous to each other and to me
- Provide me with feedback/suggestion – on how the course and my delivery can be improved
- Revise the materials you have learnt in previous course (ChE 308)

What you can expect of me

- Treat each question or concern seriously and answer these to the best of my ability

- Treat each of you with courtesy and respect

Check the website for course notes and other announcements

http://teacher.buet.ac.bd/mahammad/

Ammonia Synthesis

Textbook: No textbook

Reference book:

1. Fertilizer Manual – UNIDO
2. Ammonia Principles and Industrial practice – Max Appl, Wiley VCH 1999.
3. Fertilizer production in context of BD – Dr. Dil Afroza Berum, (Should be available in ChE library)
4. Manuals, Brochures and Leaflets of different Process Licensors, Etc.

Name of other resources will be informed when needed

Ammonia synthesis

- Uses of ammonia
- Introduction to ammonia synthesis
- Ammonia production via :
  1. Partial Oxidation (POX)
  2. Steam Reforming
- Thermodynamics aspects
- Kinetic aspects
- Process conditions

Uses of Ammonia

1. Agricultural and fertilizer industry
   - Production of ammonium phosphate, $(NH_4)_3PO_4$
   - Production of ammonium nitrate, NH_4NO_3
   - Production of ammonium sulphate, $(NH_4)_2SO_4$
   - source of protein in livestock feeds for cattle, sheep and goats
2. Nitric Acid Production – used in making explosives such as TNT
3. Ammonia-soda industry – uses ammonia for producing soda ash
4. Petroleum industry uses ammonia to
   - neutralize acid constituents of crude oil
   - protect equipment from corrosion
5. Rubber industry – prevent premature coagulation by stabilizing natural rubber
6. Pulp and paper industry – for pulping wood
7. Textile industry – manufacture of synthetic fibers such as nylon and rayon.
8. Plastics industry – manufacture of phenolics and polyurethanes.

Basic steps or works involved in establishing any chemical plants

- Feasibility studies/technology selection
- Project management
- Arrangement of financing schemes
- Financial guidance based on an intimate knowledge of local laws, regulations and tax procedures
- Environmental studies
- Basic/detail engineering
- Utilities/offsites/infrastructure
- Procurement/inspection/transportation services
- Civil works and erection
- Commissioning
- Training of operating personnel
- Plant operation/plant maintenance

Introduction to Ammonia Synthesis

- Steps in NH_3 synthesis
  - Preparation of feedstock (synthetic gas)
  - NH_3 synthesis
  - Product purification

- Stoichiometry of the reaction

$$N_2 + 3\,H_2 \rightleftharpoons 2NH_3$$

- Ammonia can be produced through a series of operations employing :
  1. Partial oxidation (POX)
  2. Gasification of heavy hydrocarbon fractions or coal
  3. Steam reforming of methane or naphtha

Introduction to Ammonia Synthesis

- Preparation of feedstock
  1. From partial oxidation of methane / naphtha
     a. Air distillation
     b. Partial oxidation of "HC" with oxygen
     c. Removal of C and recovery of heat
     d. Removal of H_2S and conversion to S
     e. Catalytic conversion of CO by steam (shift conversion)
        $CO + H_2O \rightleftharpoons CO_2 + H_2$
     f. CO_2 removal
     g. CO removal by liquid N_2

  2. From steam reforming
     a. Steam treatment (primary reforming)
     b. Conversion of residual methane by air
     c. Catalytic conversion of CO by steam
        $CO + H_2O \rightleftharpoons CO_2 + H_2$
     d. CO_2 removal
     e. CO removal

Introduction to Ammonia Synthesis

- Requirements for ammonia productions
  - To synthesize H_2, N_2
  - To remove CO, CO_2 (poison to NH_3 synthesis rxn)

i. Shift Conversion (water-gas shift rxn)

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$CO \rightleftharpoons CO_2 + C \text{ (prevent Boudouard's equilibrium)}$$

- High T-shift
  - Cat : Cr-Fe oxide catalyst
  - T : 340 – 450°C
- Low T-shift
  - Cat : Cu-Zn oxide catalyst Alumina
  - T : 200°C

ii. CO_2 removal

- Scrubbing gas with an alkaline solution, K_2CO_3 or ethanolamine

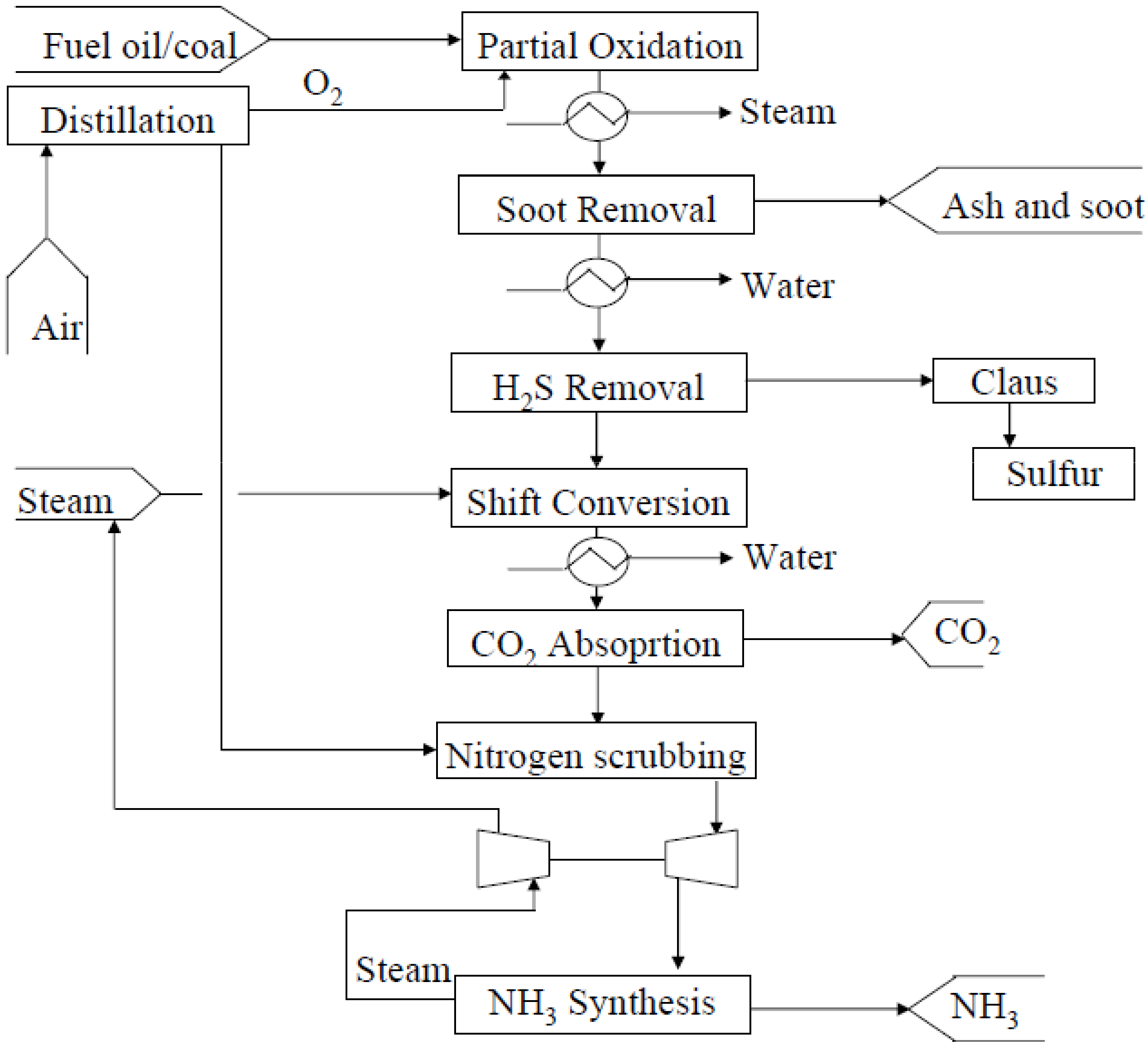
iii. Methanation

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

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

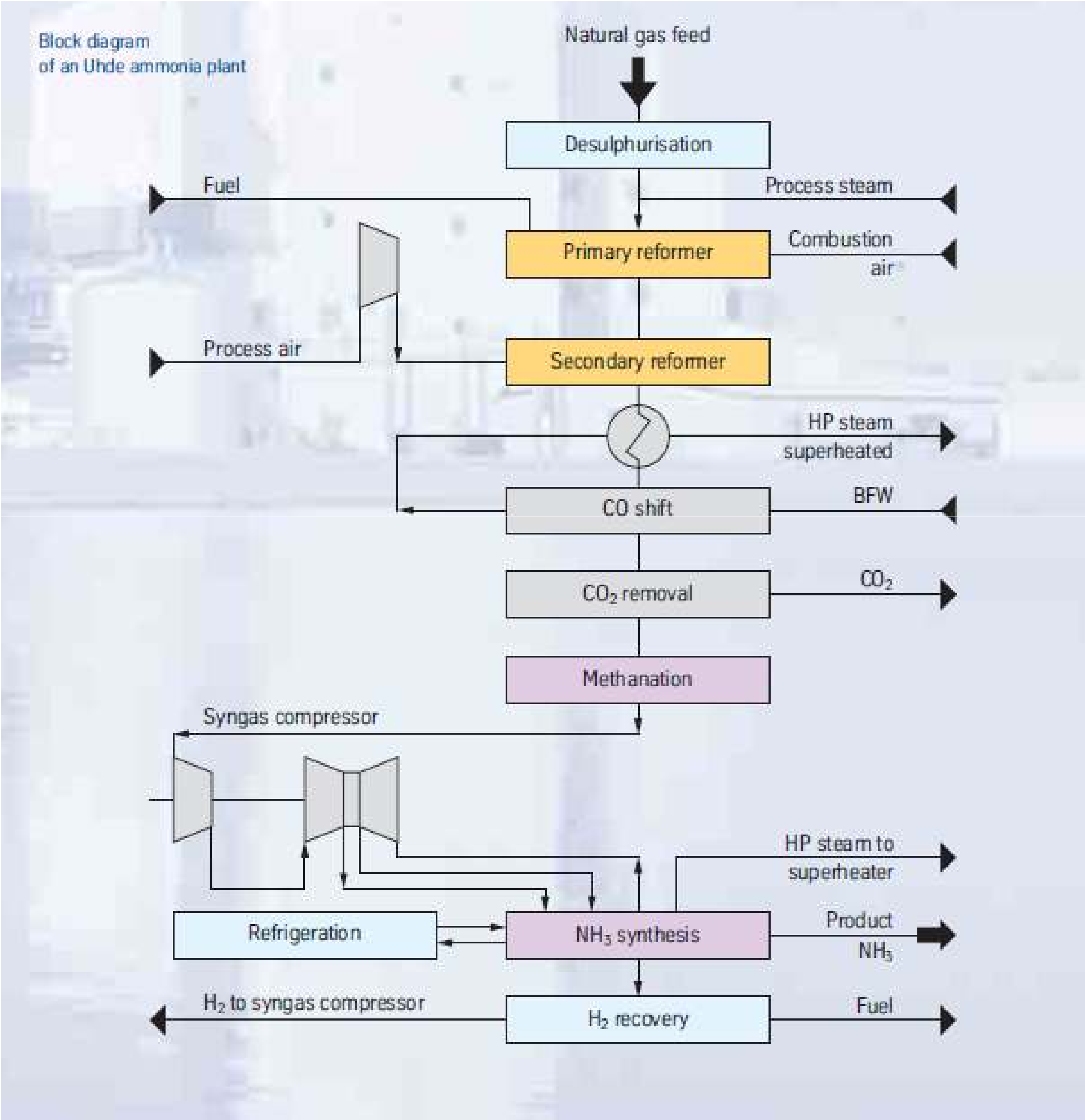
- Cat : Ni Oxide
- T : 350°C

Ammonia Production via Partial Oxidation

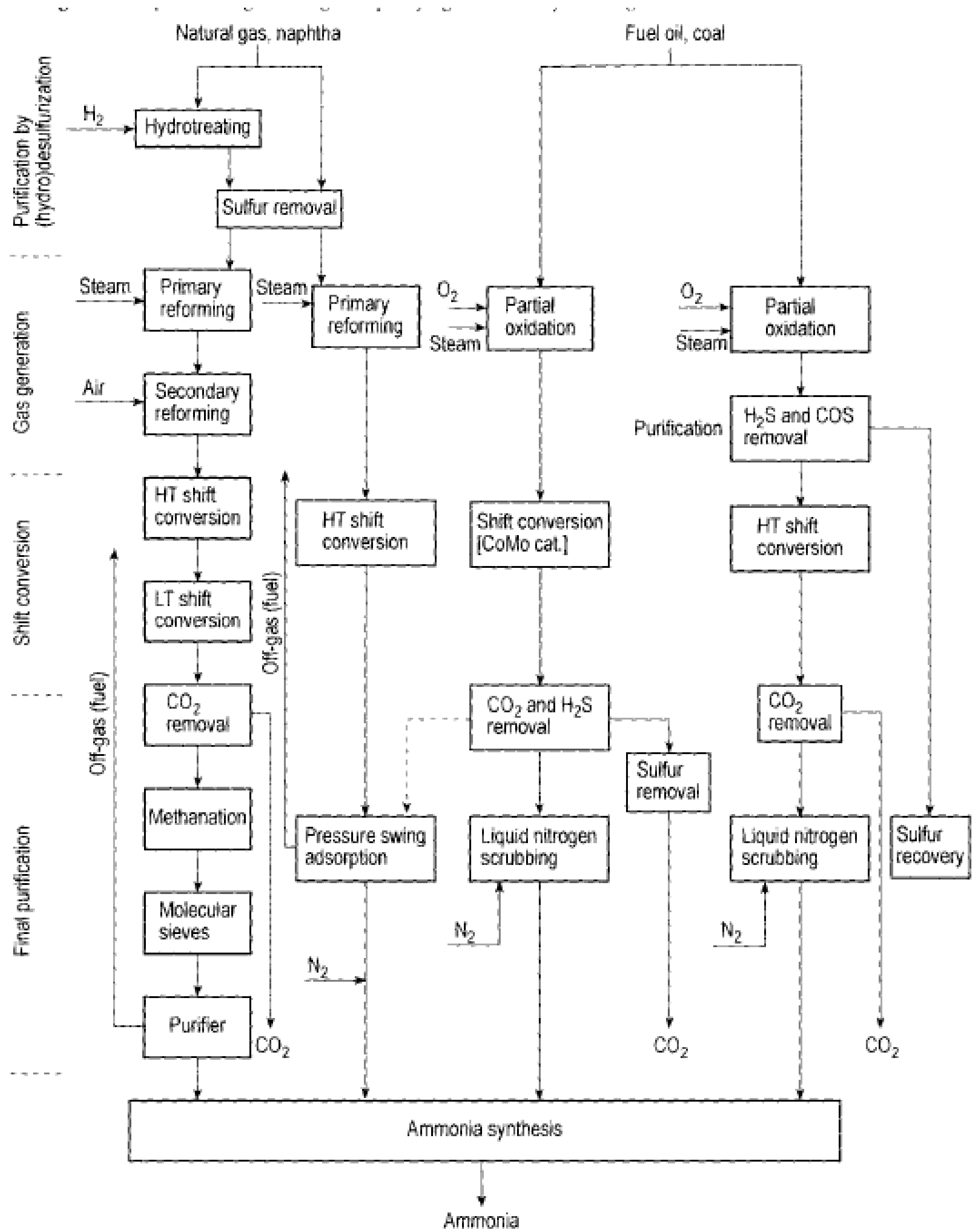


Ammonia Production Via Steam Reforming

Block diagram of UDHE ammonia plant Via steam reforming



Options for generating and purifying SynGas



Relative ammonia plant investment and relative energy requirement for 1800 t/d NH_3

	NG	Naptha	Fuel oil	Coal
Relative Investment	1	1.15	1.5	2.5
Relative specific energy requirement	1	1.1	1.3	1.7

For the natural gas based plant the current best value of relative energy requirement is 28 GJ/t NH_3, is used.

Production and consumption figures per metric ton of ammonia

Overall view of the QAFCO 4 ammonia/urea complex successfully commissioned by Uhde as early as 2004.
Capacities: 2,000 mtpd of ammonia
3,200 mtpd of urea
3,500 mtpd granulation unit

Feed and Energy Consumption		
Natural gas as feed and fuel	Gcal[1]	6.8 to 7.4
Elctric power	kWh	15 to 90
Overall feed and energy[2]	Gcal[1]	6.7 to 7.4
Utilities		
Cooling water (Δ T = 10 K)	mt	120 to 260
Demineralised water (net cons.)	mt	0.65 to 0.75
Effluents		
Treated process condensate[3]	mt	0.85 to 1.15
Product Quality		
Ammonia content	% by wt.	99.8 to 100.0
Water content	% by wt.	0.0 to 0.2
Oil content	ppm by wt.	max. 5

(1) expressed as lower heating value of natural gas per ton of ammonia
(2) electric power and steam export converted into fuel equivalents
(3) routed back to the demineralisation unit for re-use

All consumption figures are per metric ton of liquid ammonia and serve as general information only.
Local dimatic conditions and gas composition may have a considerable influence on the performance figures.

Ammonia Production via Steam Reforming

- Gas composition at outlet of primary reformer should be:
  - $(H_2 + CO)/CH_4$ = 21 to 24 by volume
- Catalyst employed : Nickel based catalyst
  - Ensure conversion of low hydrocarbon contents in a dilute medium

Primary Reforming feedstock	Natural gas		Naphtha
Post-combustion	Feedstock	Product	Product
Composition			
H_2...........................	69.30	55.30	56.10
CO..........................	9.70	13.00	10.20
CO_2..............................	10.40	7.50	11.20
CH_4.........................	10.60	0.35[(1)]	0.37[(1)]
N_2...........................	–	23.60	21.90
Ar..........................	–	0.25	0.23
Total.................	**100.00**	**100.00**	**100.00**
Air/dry gas.....................	0.41	–	0.40
H_2O/dry gas....................	0.77	0.57	0.56
Reactor exit temperature (°C)	–	1,000	1,000
Pressure (10^6 Pa absolute)......	–	3.1	1.5

Ammonia Production via Steam Reforming

- Objective – to produce ratio of CO : H_2 = 1 : 3
- Why?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

- How
  - Primary Reformer

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

    - Cat : 15% Ni alloy / alumina or Calcium aluminate
    - T : 750 – 850°C
    - P : 5 – 40 bar
  - Secondary Reformer

    $$CH_4 + O_2 \text{ (air)} \rightleftharpoons (N_2) + H_2 + CO + CO_2 + \text{traces of hydrocarbon}$$

    - Cat : lower Ni / alumina support
    - T : 1000°C
    - P : lower

Thermodynamics Aspects

- Reaction stoichiometric

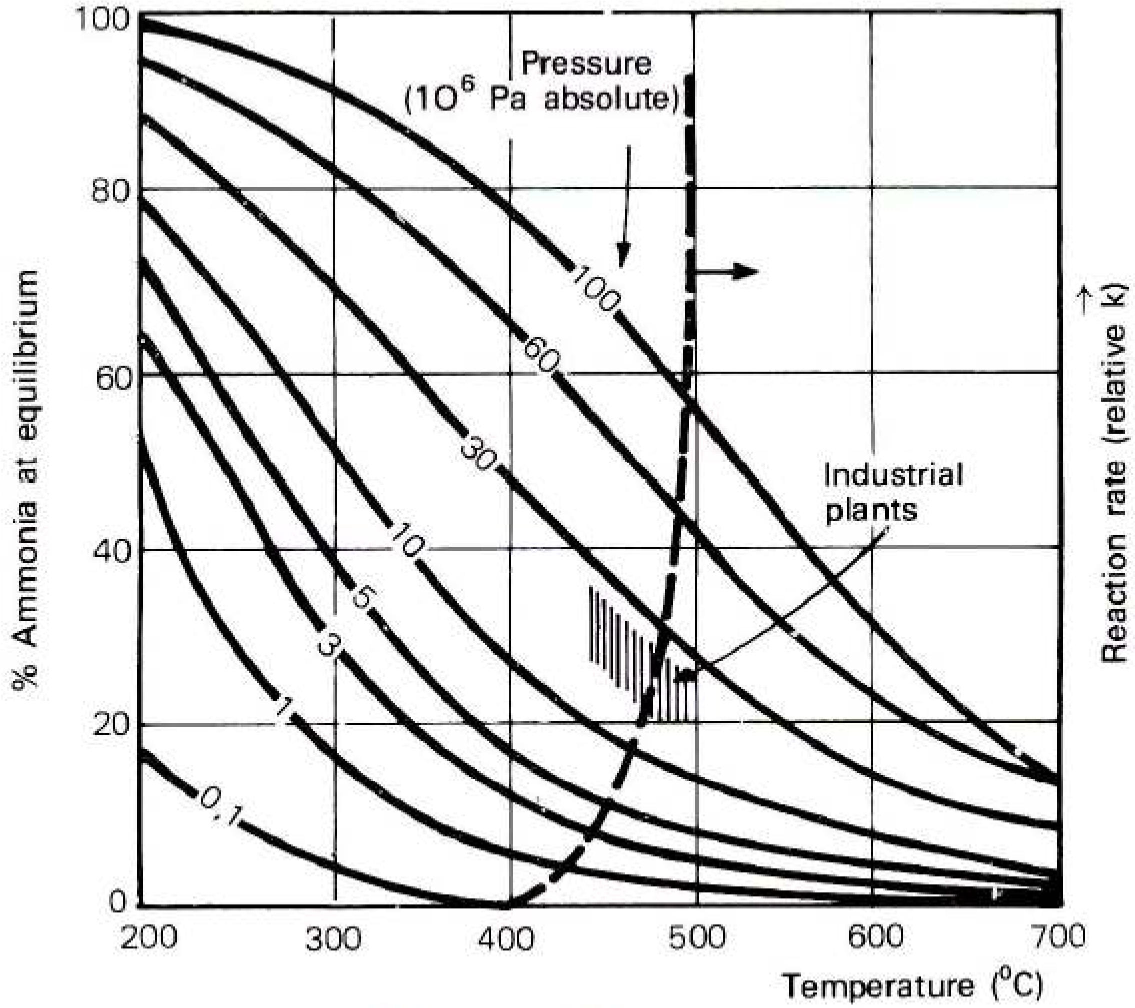
  $N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H^o_{298} = -92\ \text{kJ/mol } N_2$

  - Reaction is exothermic and endentropic
- $\Delta H^o_T = -77.24 - 54.24T + 0.19T^2$, thus
  - $\Delta H^o_{500oC} = -107.8\text{kJ/mol}$
- Equation for the equilibrium constant :

$$\lg K_p = \frac{2940}{T} - 6.178$$

- The thermodynamic considerations imply that :
  1. Once-through conversion of feed gas is limited, recycling results in synthesis loop operating at high P
  2. Partial conversion of reactants at high pressure invites large mechanical energy costs
  3. Use of low temperatures reduces reaction rate
- As can be seen from the diagram in the next slide, ammonia synthesis favors reaction at high P and low T

Thermodynamics Aspects



Equilibrium of Ammonia Synthesis

Thermodynamics Aspects

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = +46 \text{ kJ/mol}$$

- Cat : Fe based (Magnetite) promoter (Al_2O_3, K_2O, MgO, CaO)
- The reaction is sensitive to T,P

Table 1 : Yield at equilibrium at various temperature and pressure

Pressure (atm) / Temp (°C)	25	50	100	200	400
100	91.7	94.5	96.7	98.4	99.4
200	63.6	73.5	82.0	89.0	94.6
300	27.4	39.6	53.1	66.0	79.7
400	8.7	15.4	25.4	38.8	55.4
500	2.9	5.6	10.5	18.3	31.9

Kinetic Aspects

- To accelerate the approach to equilibrium, employ catalyst
  - Oxide catalysts from group 7 metals

    e.g. Fe (Fe_3O_4), promoters Al_2O_3, K_2O, SiO_2, MgO, CaO
- To improve catalyst stability, activity and resistance to poisoning
  - Ru, modified Rb, Ti, Ce compounds

- Yield (max) @ equilibrium : High P & Low T (according to thermodynamics)

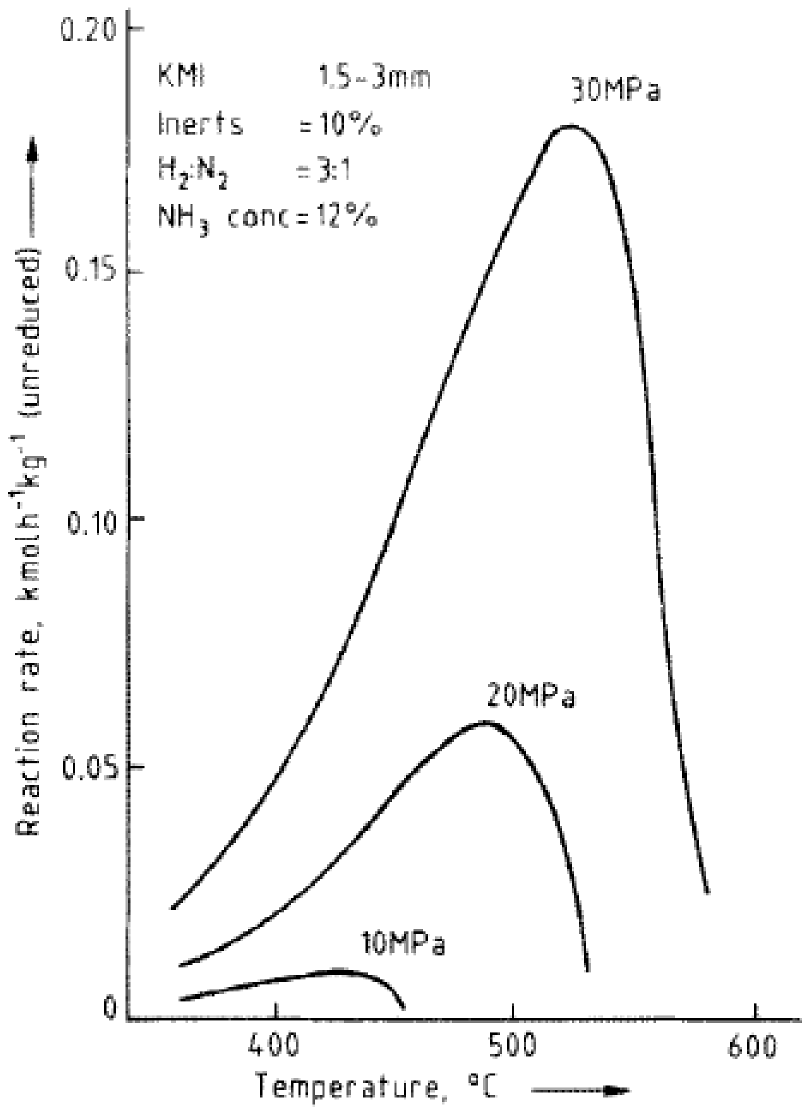
- Operating condition
  - P : 150 – 350 atm
  - T : 400 – 550°C (according to kinetics)

    - to achieve acceptable conversion

- Catalyst for NH_3 synthesis
  1. Fe based / Al_2O_3 and/or K_2O, MgO, CaO (Magnetite)
  2. Ni oxide / Al_2O_3 or $CaAl_2O_4$
  - T = 650 – 850°C

Kinetic Aspects

Reaction rate for NH_3 synthesis.
Dependence on the temperature at various pressure.



Basic Features of Ammonia Synthesis Loop

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad \Delta H = -92.44\ \text{kJ/mol}$$

- **Limited by unfavorable thermodynamic condition(25%-35%)**
  - Ammonia is separated by condensation from unreacted gas
  - Unconverted gas is supplemented by fresh synthesis gas and is recycled back to converter
  - The concentration of the inert gases (CH_4, Ar) is controlled by a small continuous purge gas
- **Properties of synthesis catalyst and Mechanical restrictions govern the design of ammonia converter and layout of synthesis loop**
- **Evaluation criteria are energy consumption, investment and reliability**

Synthesis loop configurations

Figure: **Schematic flow diagrams of typical ammonia synthesis loops**

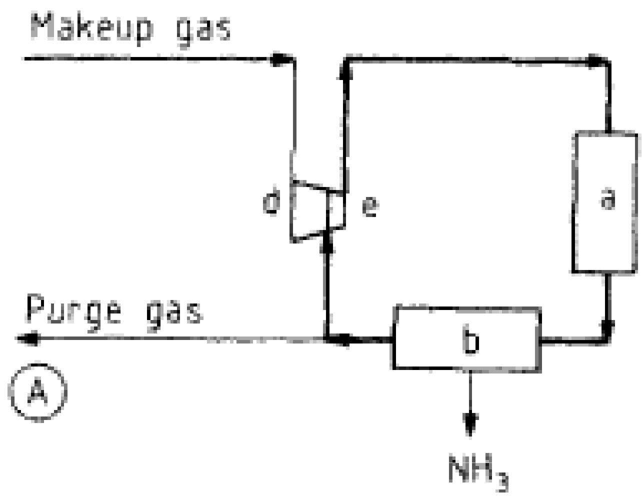
a) Ammonia converter with heat exchangers

b) Ammonia recovery by chilling and condensation

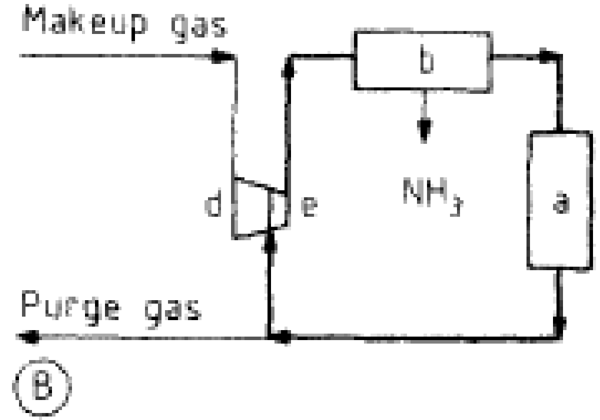
c) Ammonia recovery by condensation at ambient temperature

d) Synthesis gas compressor

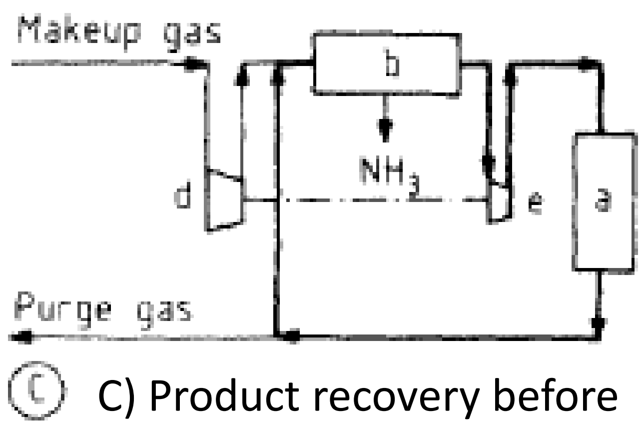
e) Recycle compressor



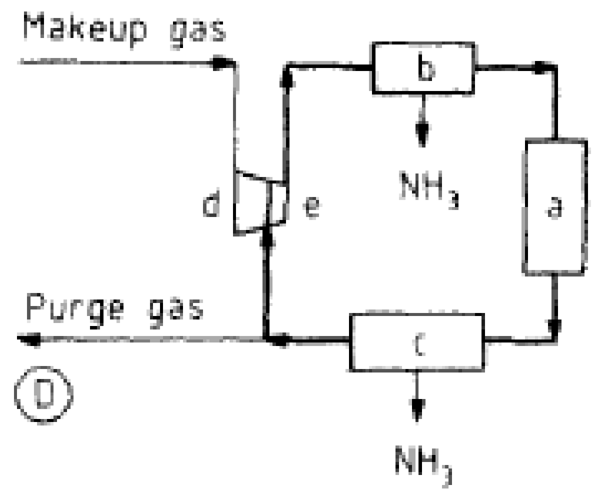
A) Synthesis loop for pure and dry makeup gas



B) Product recovery after recycle compression

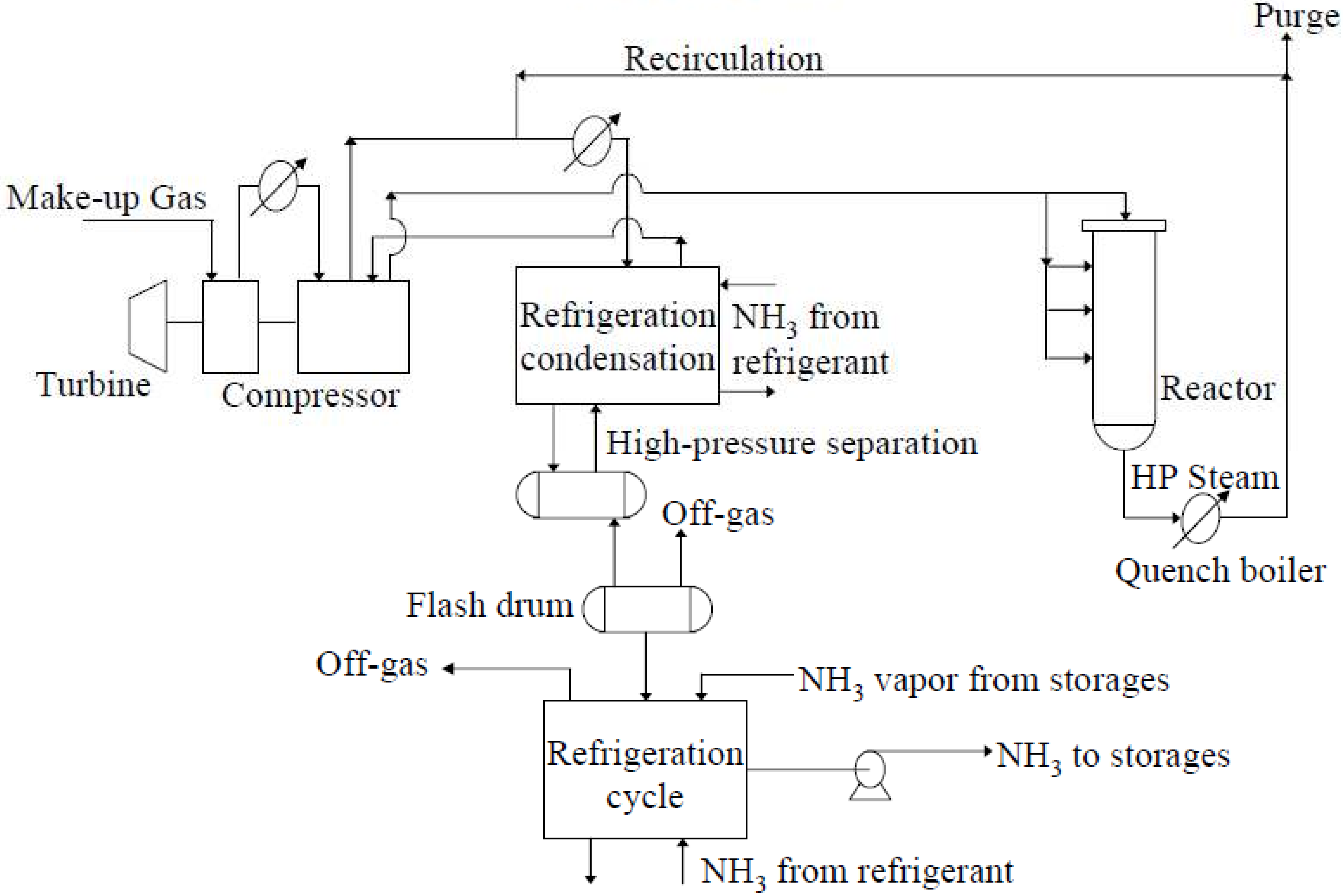


C) Product recovery before recycle compression (four-nozzle compressor design



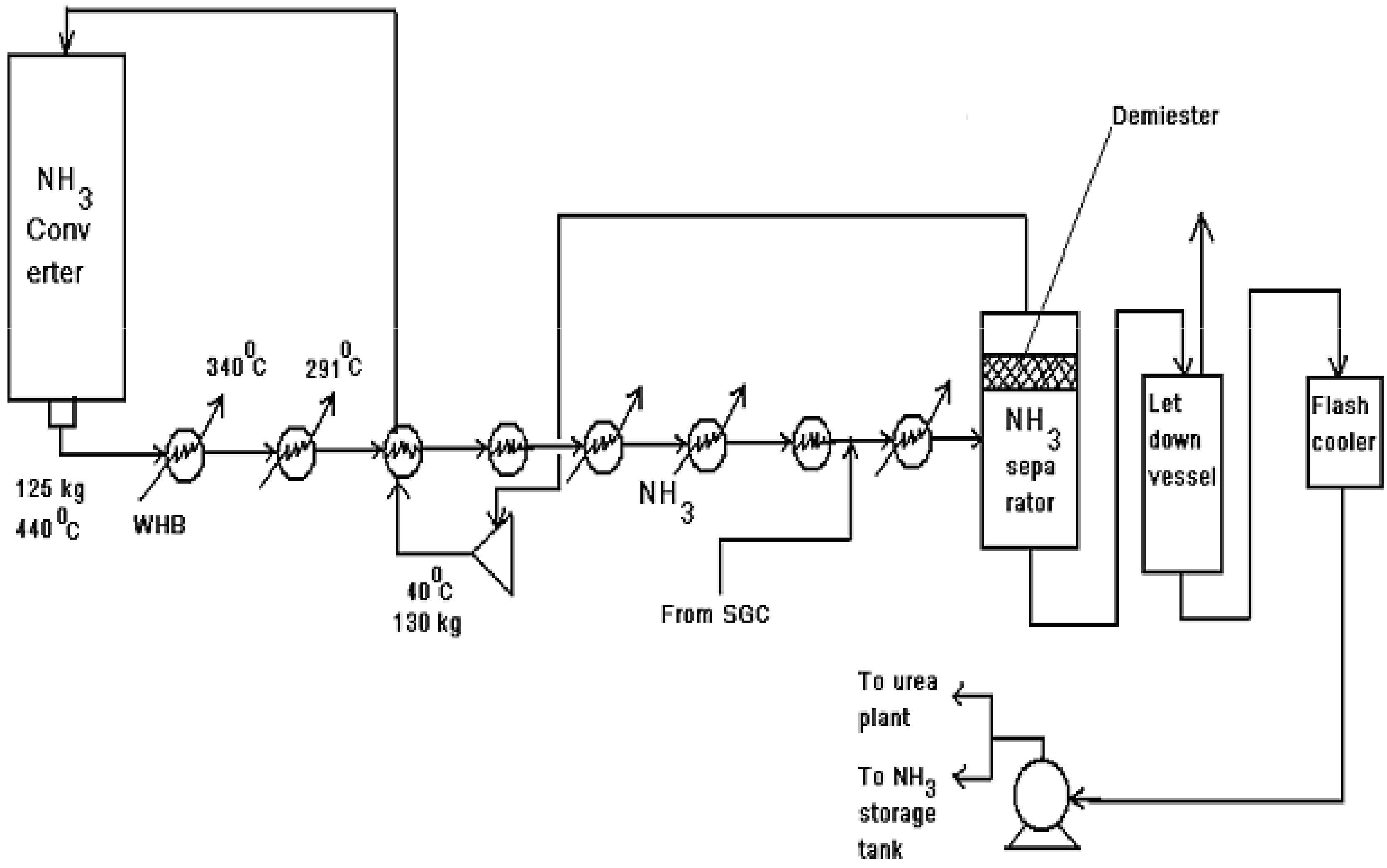
D) Two stages of product Condensation

Process

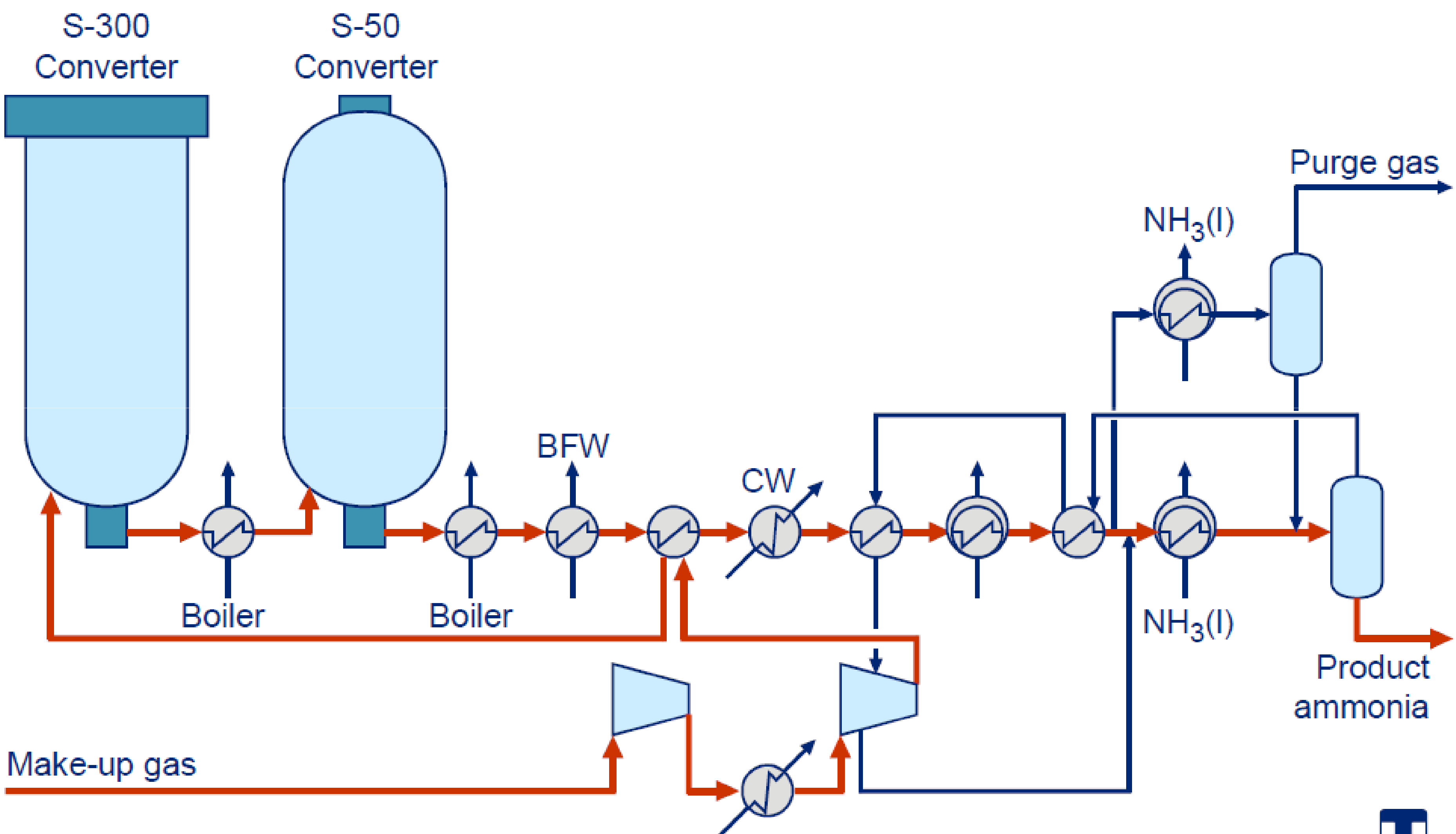


Base scheme of ammonia synthesis loop

KAFCO's synthesis and refrigeration loop



S-350 ammonia synthesis loop



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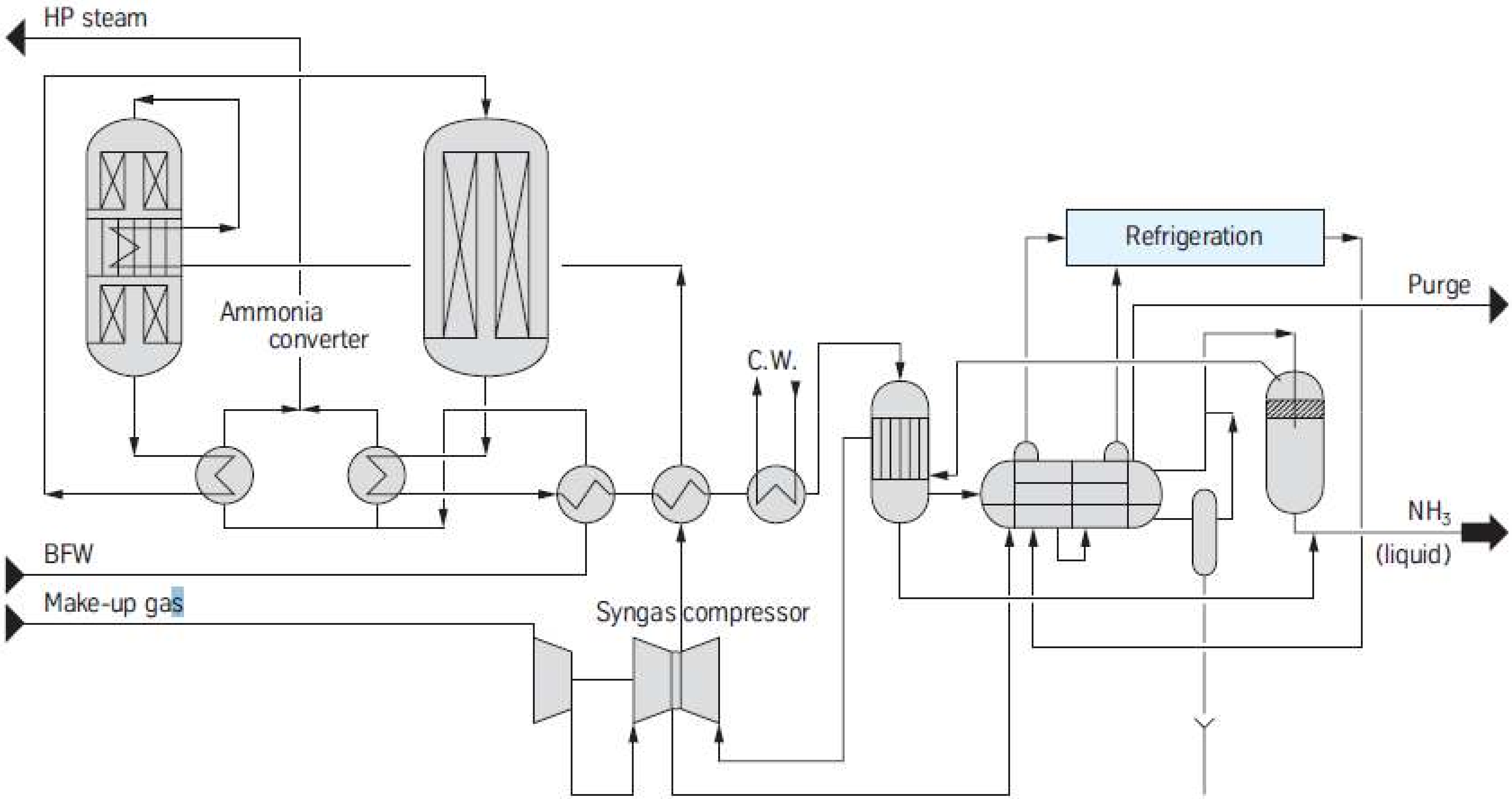
Uhde's Synthesis and refrigeration loop



Example: SAFCO IV; ZFCL is similar but 1 reactor

Ammonia Converter

- Standard method for ammonia synthesis :
  1. Multi stage centrifugal compressor driven by steam turbin – pressurizes fresh feed and recycle gasses
  2. Multi-layer reactor, vertical with axial stream flow designed to preheat feed and remove heat generated from reaction
  3. A train of heat exchanger and high-pressure separator – to obtain liquid ammonia and recirculate unconverted gases to the compressor
  4. An NH_3 refrigeration cycle by Joule Thompson compression/expansion comprising three stages – 13.5, -7.5 and 33.5^oC to liquefy the ammonia produced to around -23.5^oC

Process Conditions

- Characteristics of a conventional Reactor
  - Unit production capacity…………… 1200 tonne/day (t/day)
  - Operating condtion……………….... 35×10^6 Pa abs
  - Weight…………………………….... 386tonne (t)
  - Catalyst volume…………………..... $36m^3$
  - Shell length……………………….... 22m
  - Shell diameter……………………… 2m

- Three generations of reactor technology development can be distinguished and is given in the table in the next slide

- Latest improvements in ammonia production by steam reforming of natural gas are :
  a) ICI/AMV process – excess air in the secondary reforming step
  b) The Fertimont process
  c) Byas technology – direct introduction of part of feed in secondary reforming step
  d) KTI Parc technique – low capacity installations

Gen.	Reactor Type	Cooling type	Companies / Licensors	Process Conditions
1^{st}	Vertical shell & tube heat exchanger	External (shell)	Ammonia Casale & TVA	Pressure : 30 - 35 × 10^6 Pa abs Capacities : 600 t/day
	Vertical, multiple bed, intermediate cooling	Injection of quenching gas	BASF	
		Water tubes & steam production	Montecatini & OSW	
2^{nd}	Vertical, multiple catalyst beds (usually two), Axial flow.	Injection of quenching gas	Kellog *(figure A) Topsoe, ICI & Ammonia Casale	Pressure : 20 to 25 × 10^6 Pa abs Capacities: 1500 t/day
		Water tubes and steam production	Uhde& Montedison	
	2 shells, 1intermediate external heat exchanger	Water tubes and steam production	C.F. Braun	
3rd	Horizontal system, axial flow, catalyst bed	Quenching by gas injection	Kellogg *(figure B)	Low ΔP
	Vertical, radial flow catalyst bed	Built in gas/gas exchanger	Topsoe	—
	Vertical, axial and Radial flow, catalyst bed with high catalyst volumes	—	Ammonia Casale	Pressure : $< 5 \times 10^6$ Pa abs

TVA : Tenneessee Valley Authority
OSW : Österreichische Stickstoff Werke

*Figures A and B are shown in the next slide

Process Conditions

- Process for ammonia synthesis started of with high pressure operation (30 to 35 × 10^6 Pa abs)
- Low pressure process is subsequently adopted 20 to 25 × 10^6 Pa abs
- Subsequently, operation can be carried out at 15 to 20 × 10^6 Pa abs with very pure feed including liquid nitrogen scrubbing
- ICI, SNAM Progetti (Societa Nazionale Metanodotti) and Pullman-Kellogg recommends operation at 5 × 10^6 Pa abs
  - enhance energy optimization but
  - requires larger catalyst loading and higher unconverted gas recirculation rates
- Temperature range of operation : 480 to 550°C

Reactor for Ammonia Synthesis

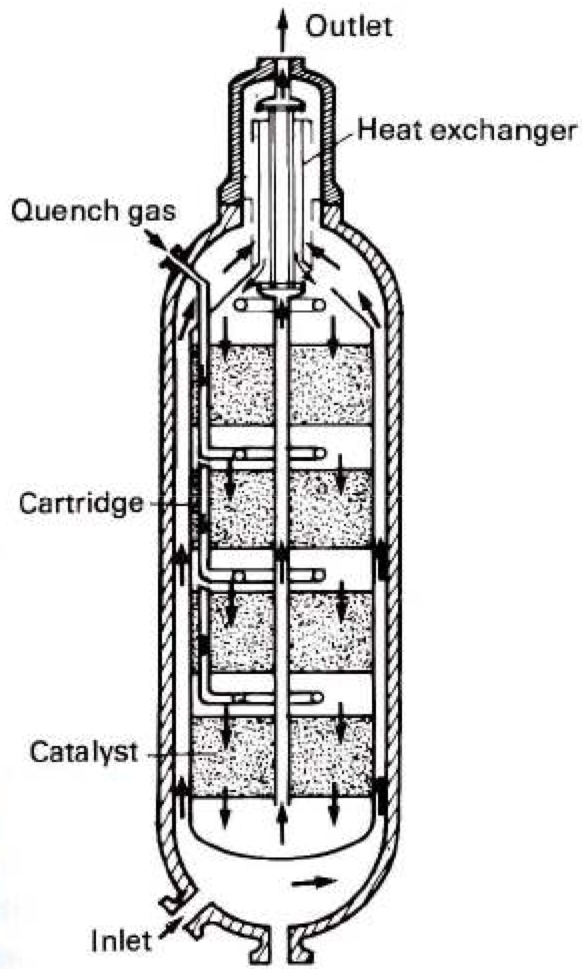


Figure A : Kellogg reactor - 2nd generation

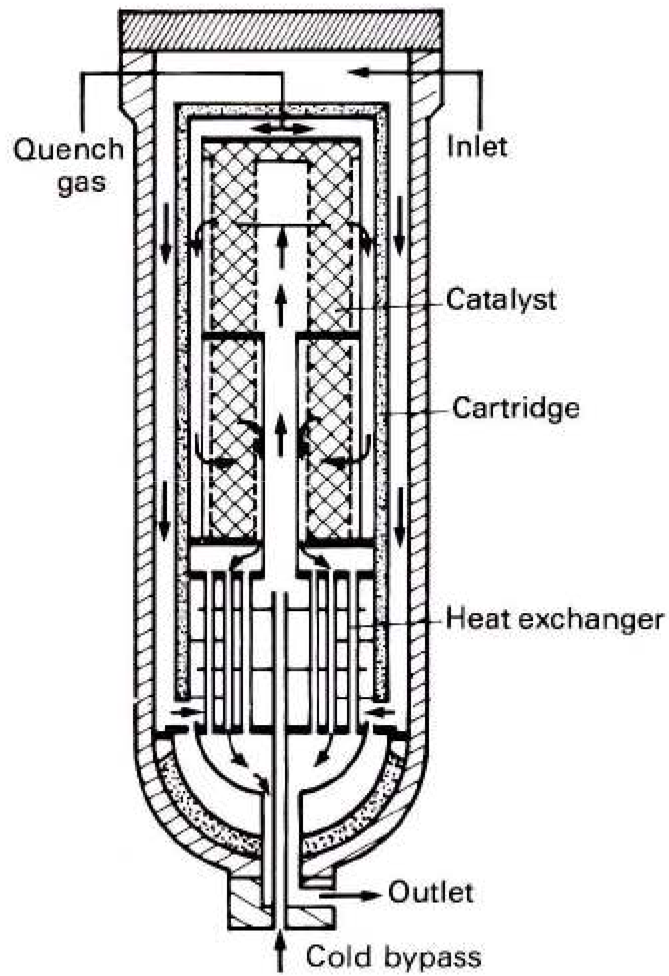
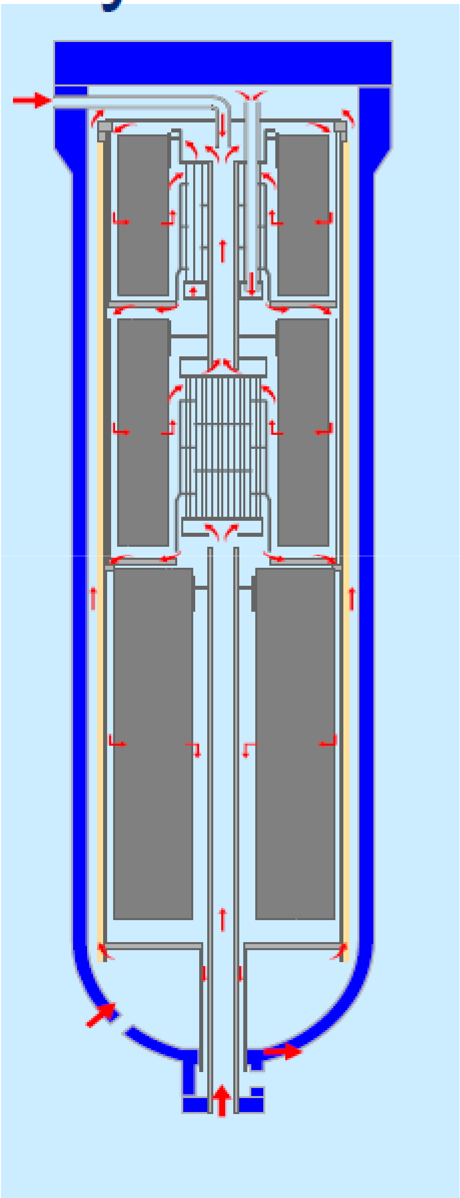


Figure B : Topsoe's reactor 3rd generation

S-300 ammonia synthesis converter



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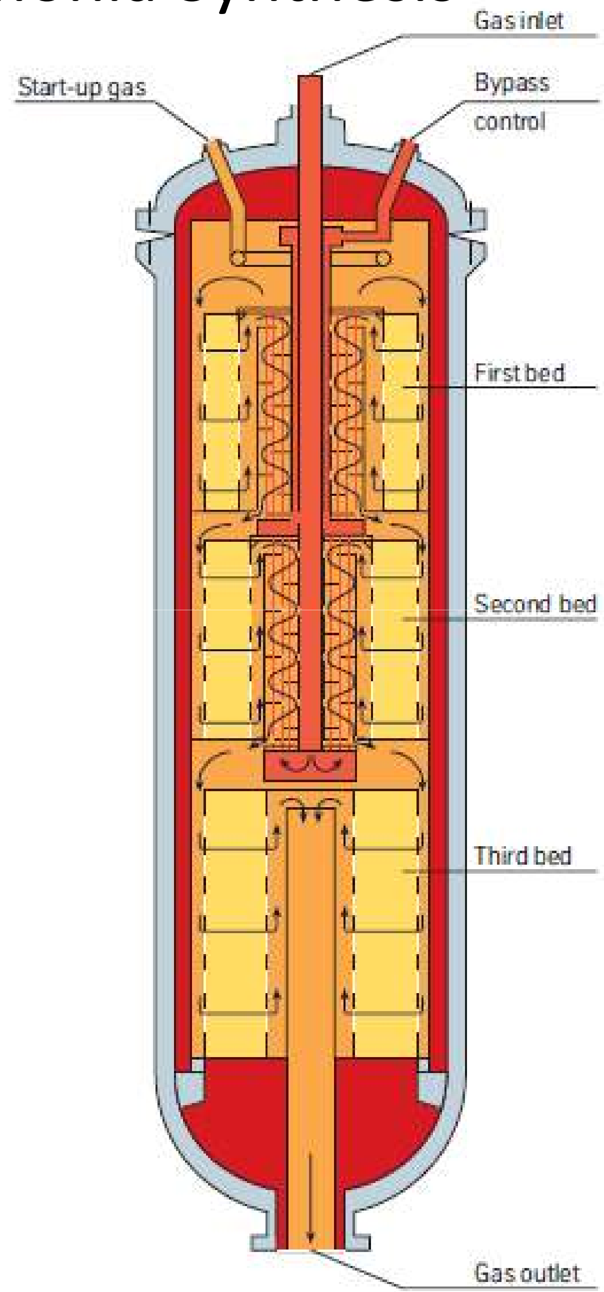
Reactor for Ammonia Synthesis

Uhde's latest



Performance of converter

- Optimum pressure 150-250 bar

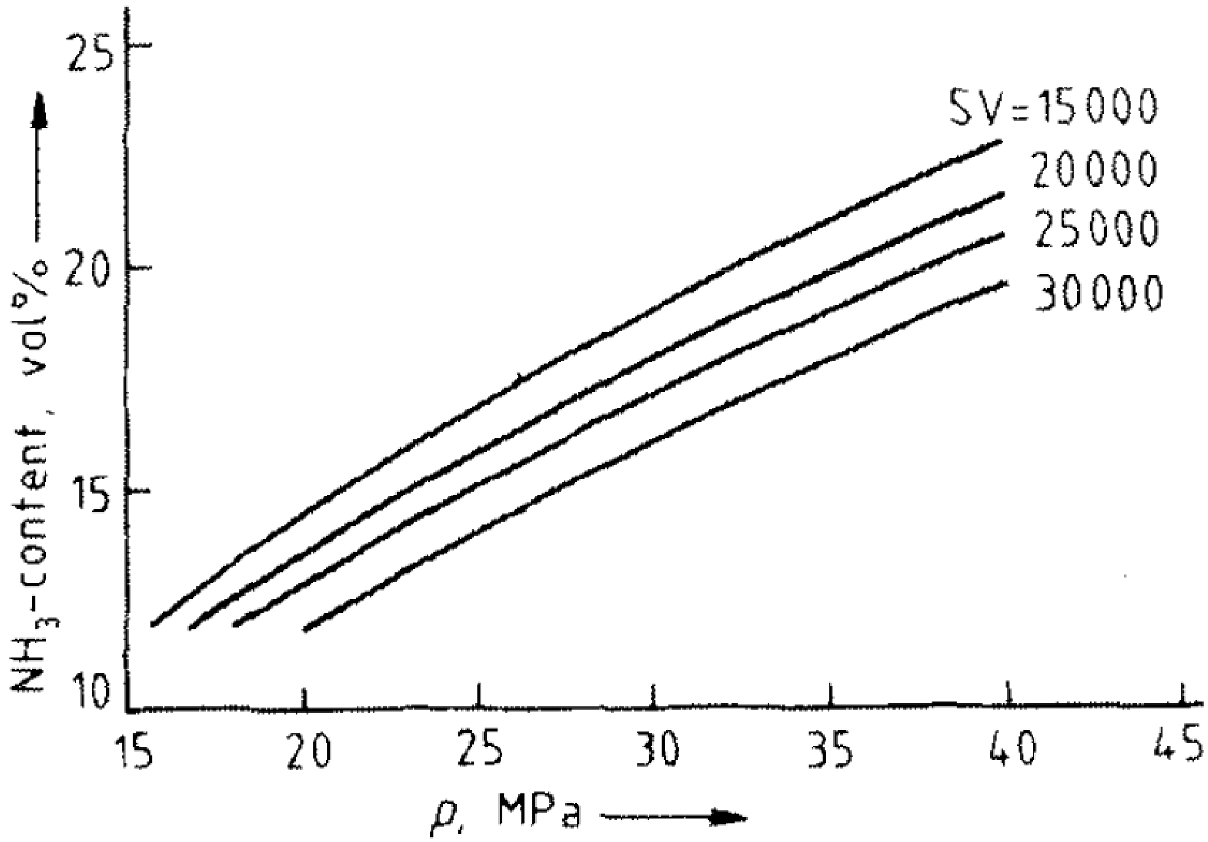


Figure: performance of a 4 bed quench converter as a function of operating pressure with space velocity(per hour) as parameter, 10% inert in the gas.

Performance of converter

- Inert content 0-15 vol%.

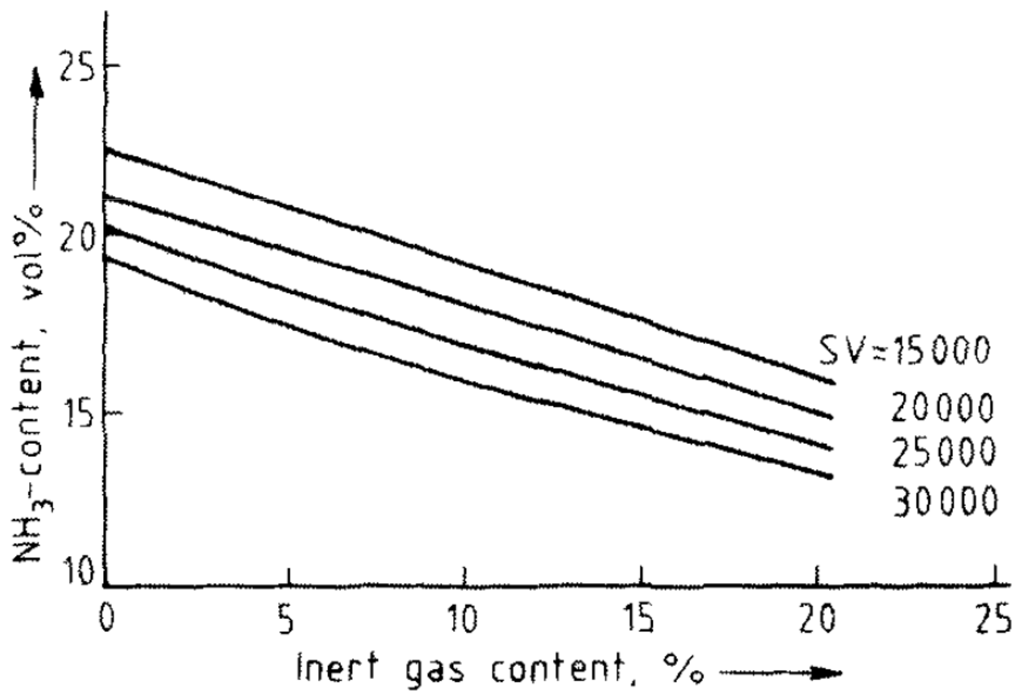


Figure: Performance of a converter as a function of inlet inert gas (CH_4 and Ar) content with space velocity (per hour) as parameter, inlet NH_3 content is 3.5%; 30 MPa pressure; catalyst particle size is 6 - 10 mm.

Performance of converter

- Oxygen content , not more than 10 ppm in make up gas or 3 ppm in the converter inlet.

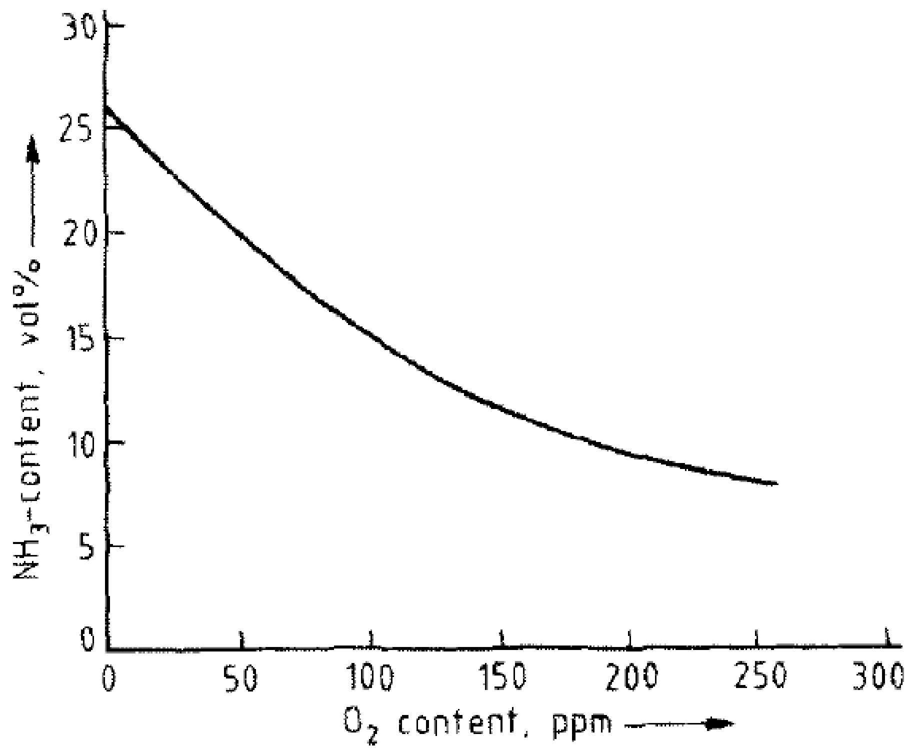


Figure: Performance of a converter as a function of oxygen content (all oxygen-containing impurities) in the inlet synthesis gas

Performance of converter

- Optimum H_2/N_2 ratio is 2 at high space velocity (SV) and 3 at low space velocity. (12000-35000)