

TOPSOE AMMONIA PROCESS

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1. Introduction:

The industrial synthesis of ammonia is the bedrock of the global fertilizer industry and a critical component of the emerging hydrogen economy. While the fundamental chemistry is based on the Haber-Bosch process developed in the early 20th century, modern implementations have drastically improved efficiency and scale.

This report focuses on the **Haldor Topsoe Ammonia Process**, a market-leading technology characterized by its proprietary catalyst formulations, radial flow converter designs (S-200/S-300), and the advanced SynCOR™ autothermal reforming technology. This section outlines the theoretical underpinnings and global process architecture, setting the stage for the detailed unit operation analysis of the separation and compression backend.

2. Theoretical Background:

2.1 Fundamental Chemistry

The core transformation is the exothermic reaction of nitrogen and hydrogen over a promoted iron catalyst.



Due to the significant reduction in molar volume (4 moles of reactant to 2 moles of product), the reaction equilibrium is favored by **high pressure** and **low temperature** (Le Chatelier's Principle). However, the strong triple bond of Nitrogen creates a kinetic barrier, requiring high temperatures (300 – 500 °C) to activate the reaction at an industrial rate.

2.2 Reforming Chemistry

Before synthesis, hydrogen is generated via reforming. In the advanced SynCOR™ configuration, this occurs via Autothermal Reforming (ATR), combining partial oxidation and steam reforming:



Topsoe's SynCOR™ operates at an ultra-low steam-to-carbon (S/C) ratio of **0.6**, significantly reducing steam throughput compared to conventional SMR (S/C ~3.0), resulting in lower capital and operational costs.

2.3 Topsoe Catalyst Technology

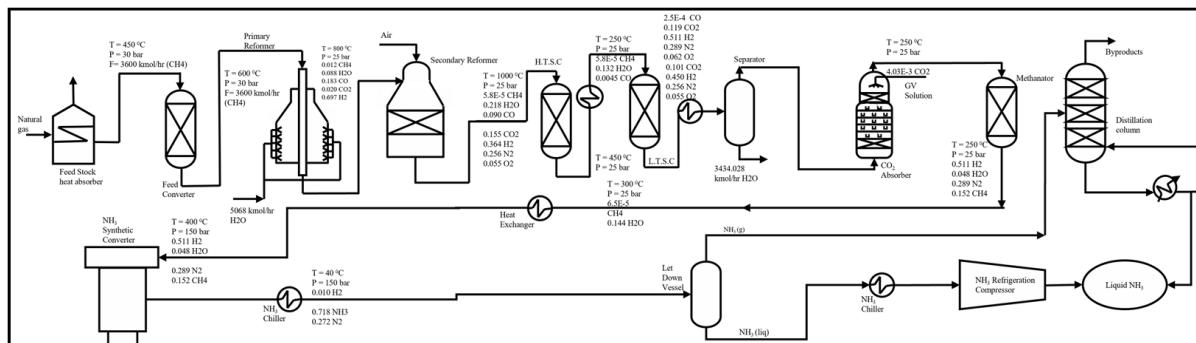
The efficiency of the Topsoe process relies heavily on the **KM Catalyst Series**.

KM1 (Iron-Based): The industry standard multipromoted magnetite catalyst (Fe_3O_4 with Al_2O_3 , K_2O). It offers high activity and mechanical strength.

This catalyst is optimised for the Radial Flow Converter design, enabling the use of smaller particles (1.5–3.0 mm). Smaller particles increase the geometric surface area available for reaction without incurring the high-pressure drop penalty associated with axial flow reactors.

2.4 Process Flowsheet Description

The integrated plant operates in a sequential flow, preparing the syngas before it enters the high-pressure synthesis loop.



2.4.1 Front-End (Gas Generation)

Desulfurization: Feedstock passes through ZnO beds to remove sulfur poisons ($\text{H}_2\text{S} < 0.1\text{ppm}$)

Reforming (SynCOR™): Oxygen-fired reforming produces raw syngas at $950 - 1000^\circ\text{C}$.

Shift Conversion: High-Temperature Shift (HTS) and Low-Temperature Shift (LTS) converters maximize hydrogen yield.

CO₂ Removal & Methanation: CO₂ is stripped (typically using amine-based solutions), and residual carbon oxides are converted back to methane to prevent poisoning the ammonia synthesis catalyst.

2.4.2 The Synthesis Loop (Back-End)

This is the critical section where conversion and recovery occur.

Compression: Syngas is compressed to 150–250 bar.

Synthesis (Converter S-300): The 3-bed radial converter achieves 15–20% conversion per pass.

Heat Recovery: Waste heat generates High-Pressure (HP) steam.

Separation: The loop utilizes a **Letdown Vessel** and **Distillation Column** to separate liquid ammonia from unreacted gases.

Recycle: Unreacted hydrogen and nitrogen are recompressed and returned to the reactor.

3. Separation Fundamentals:

Before diving into the specific unit operations, it is essential to understand the physical principles driving these separations.

3.1 Flash Separation (The Letdown Vessel)

The Letdown Vessel functions as a pressure reducing valve followed by a settling tank. By dropping the pressure significantly, the mixture enters a two-phase region:

- **Vapor Phase:** Light gases (Hydrogen, Nitrogen, Methane) escape.
- **Liquid Phase:** Heavier Ammonia condenses and collects at the bottom.

This process is modeled using the Rachford-Rice Equation to solve for the vapor fraction:

$$F = \sum_i \frac{z_i(K_i - 1)}{1 + \mathcal{V}(K_i - 1)} = 0$$

3.2 Distillation (The Purification Column)

Distillation exploits the difference in volatility between components. In this specific case, we are separating Ammonia (volatile) from heavier residues (water/byproducts). We utilize the

McCabe-Thiele Method, a graphical approach that determines the number of equilibrium stages required based on the reflux ratio and feed conditions.

3.3 Compression Thermodynamics

The compressor increases the pressure of low-pressure vapor to facilitate condensation. Performance is governed by the compression ratio (P_{out}/P_{in}) and isentropic efficiency, ensuring the mechanical energy input effectively raises the gas potential for downstream condensation.

3.4 Unit Operation I: Letdown Vessel & Separator

The recovery process begins with stabilizing the high-pressure output from the reactor.

3.4.1 Letdown Vessel (LDV) Performance

The LDV operates adiabatically. The rapid expansion of gas results in a significant temperature drop due to the Joule-Thomson effect.

- **Inlet Conditions:** The feed enters at **373.15 K** and **100 bar**.
- **Flash Conditions:** Pressure is reduced to **20 bar**, causing the temperature to drop to **294.0 K**.
- **Phase Split:** This pressure drop achieves a near-perfect equilibrium split:
 - **Vapor Fraction:** 0.5029 (50.29%)
 - **Liquid Fraction:** 0.4971 (49.71%).

3.4.2 Separator Analysis

The upstream Separator operates at **220.0K** and **25 bar**. Mole fraction analysis confirms high recovery efficiency; non-condensables like H₂ ($y=0.4701$) and N₂ ($y=0.2800$) preferentially remain in the vapor phase, leaving the liquid rich in product.

3.4.3 Energy Balance

Enthalpy calculations across the vessels confirm the adiabatic nature of the operation ($Q=0$). The total enthalpy of the feed matches the sum of the product enthalpies, validating the energy balance model.

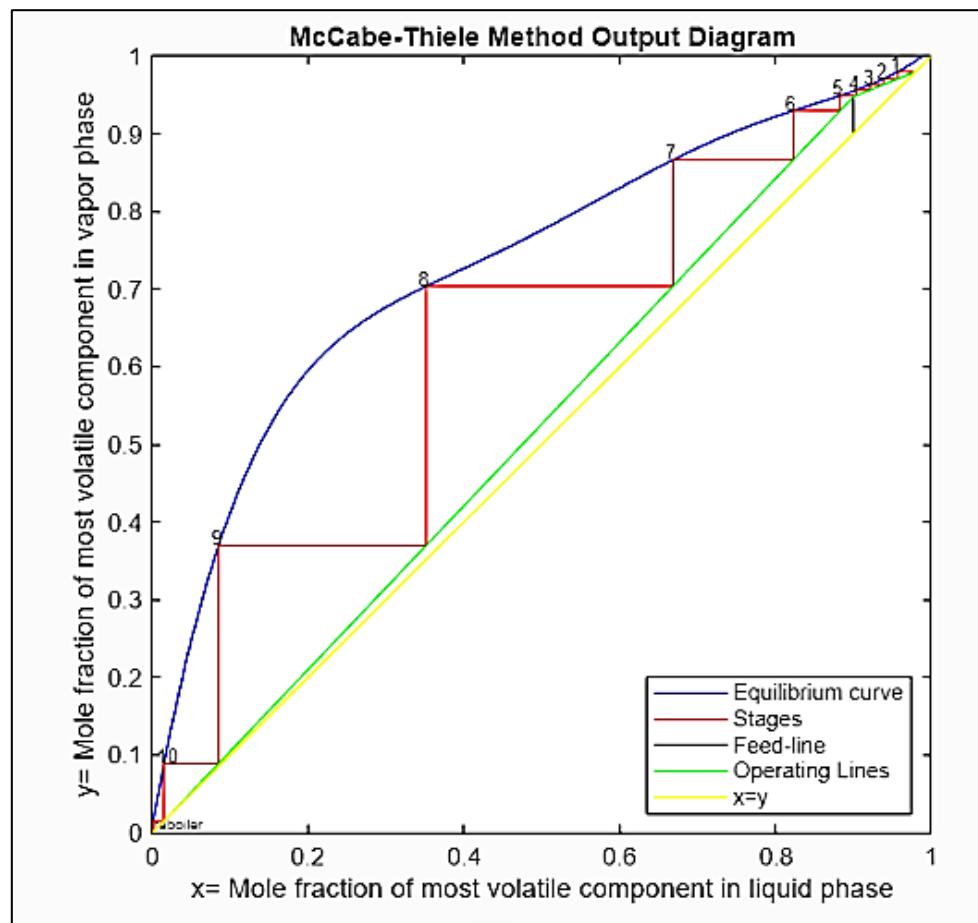
Section	Total Liquid Enthalpy	Total Vapor Enthalpy	Net Latent Heat Effect	Total Feed enthalpy	Total Product Enthalpy
Separator	539.9	3833.8	3293.9	4373.7	4373.7
Letdown Vessel	100.6	2939.7	2839.1	3040.3	3040.3

3.5. Unit Operation II: Distillation Column

The liquid stream from the LDV enters the distillation column for final purification.

3.5.1 McCabe-Thiele Analysis

The graphical analysis defines the theoretical stages required. The Operating Lines (Enriching and Stripping) intersect the Equilibrium Curve to map the separation process.



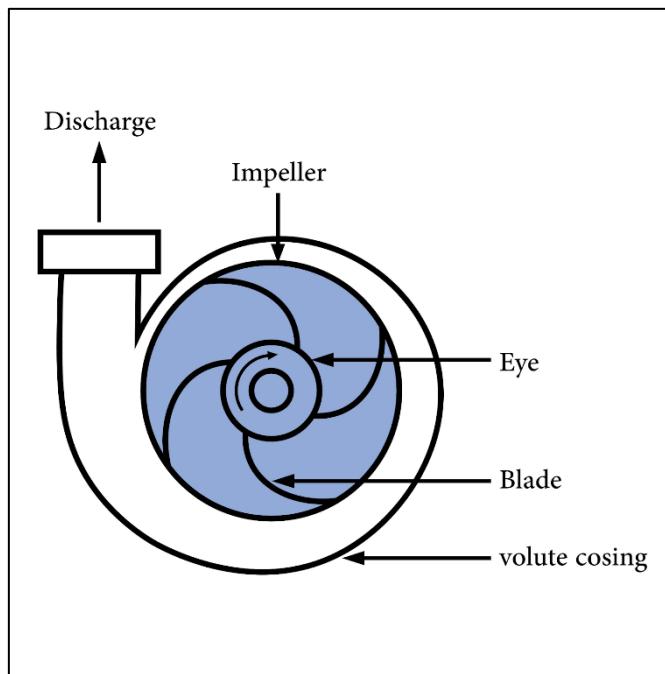
3.5.2 Design Specifications

The simulation yields the following design parameters:

- **Throughput:** Distillate (D) flow is **183.5 kmol/hr**, with Bottoms (B) at **16.5 kmol/hr**.
- **Staging:**
 - **Minimum Stages (N_min):** 7 stages (at infinite reflux).
 - **Theoretical Equilibrium Stages (NTP):** 11 stages are required for operation.
 - **Feed Location:** Optimal feed point is at **Stage 5**.
- **Reflux:** The minimum reflux ratio (R_{min}) is **0.455**, indicating a favorable separation due to high relative volatility.

3.6 Unit Operation III: Refrigeration Compressor

The compressor recovers low-pressure ammonia vapor, pressurizing it for condensation and storage.



3.6.1 Operating Conditions

- **Inlet (Suction):** Pure Ammonia vapor (NH_3) enters at **245.1 K** and **2.0 bar**.
- **Outlet (Discharge):** The gas exits at **400.76 K** and **10.0 bar**.

3.6.2 Performance Metrics

- **Compression Ratio:** The unit achieves a ratio of **5:1** (10 bar / 2 bar).
- **Thermal Effect:** The process generates significant heat, raising the fluid temperature by **155.6 C**. This necessitates downstream cooling/intercooling.
- **Work Input:** The specific work of compression is calculated at **179.98 kJ/kg**.
- **Compressibility:** With an average Z-factor of 0.9971, ammonia behaves nearly ideally under these suction/discharge conditions.

3.7 Conclusion

The detailed simulation of the Topsoe Ammonia Synthesis backend confirms an efficient design:

1. **Separation:** The Letdown Vessel effectively sheds 50% of the stream as vapor, removing non-condensables.
2. **Purification:** The Distillation Column meets product specs with only 11 theoretical stages and a low reflux ratio.
3. **Recovery:** The Compressor efficiently upgrades waste vapor (2 bar) to condensable gas (10 bar), closing the loop.

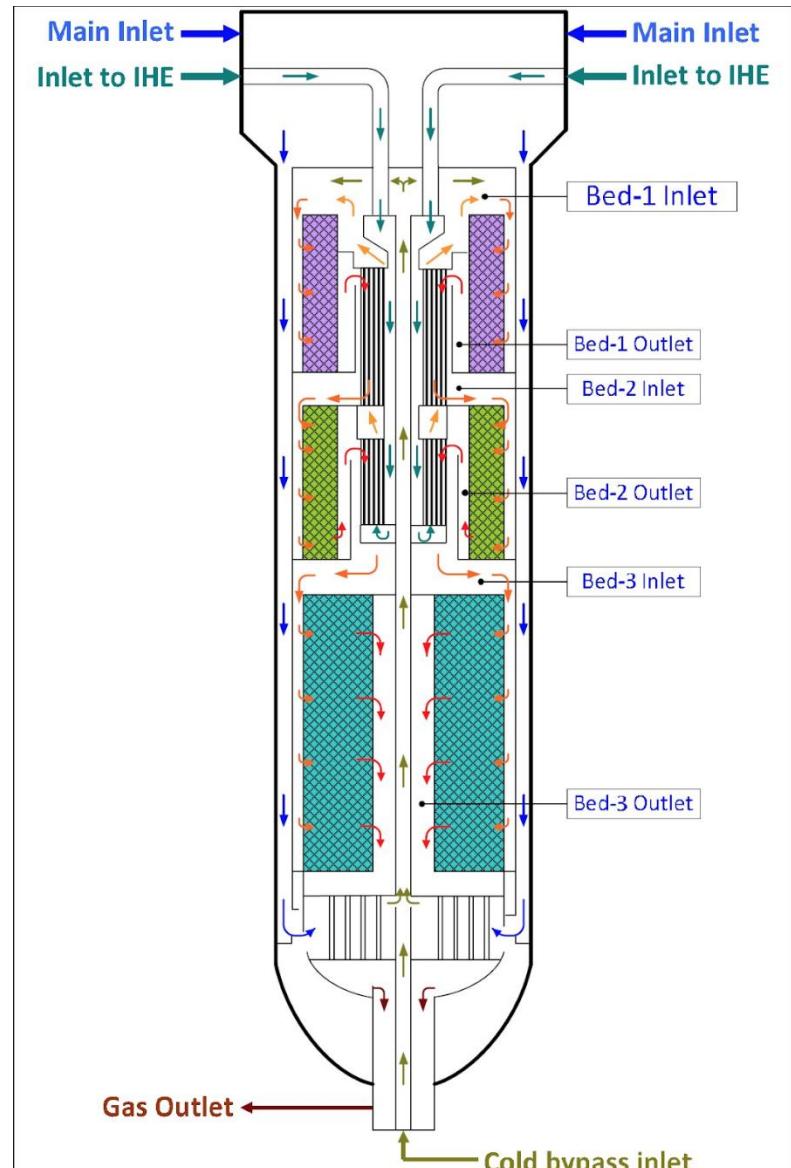
4. Reaction Kinetics:

- The intrinsic kinetics of ammonia synthesis are well described by the Temkin-Pyzhev rate expression, which accounts for the strong inhibitory influence of ammonia on the catalyst surface.
- The rate constant exhibits Arrhenius dependence, and diffusion limitations within porous iron catalysts reduce the observed rate by an effectiveness factor typically between **0.6** and **0.85** under industrial conditions.

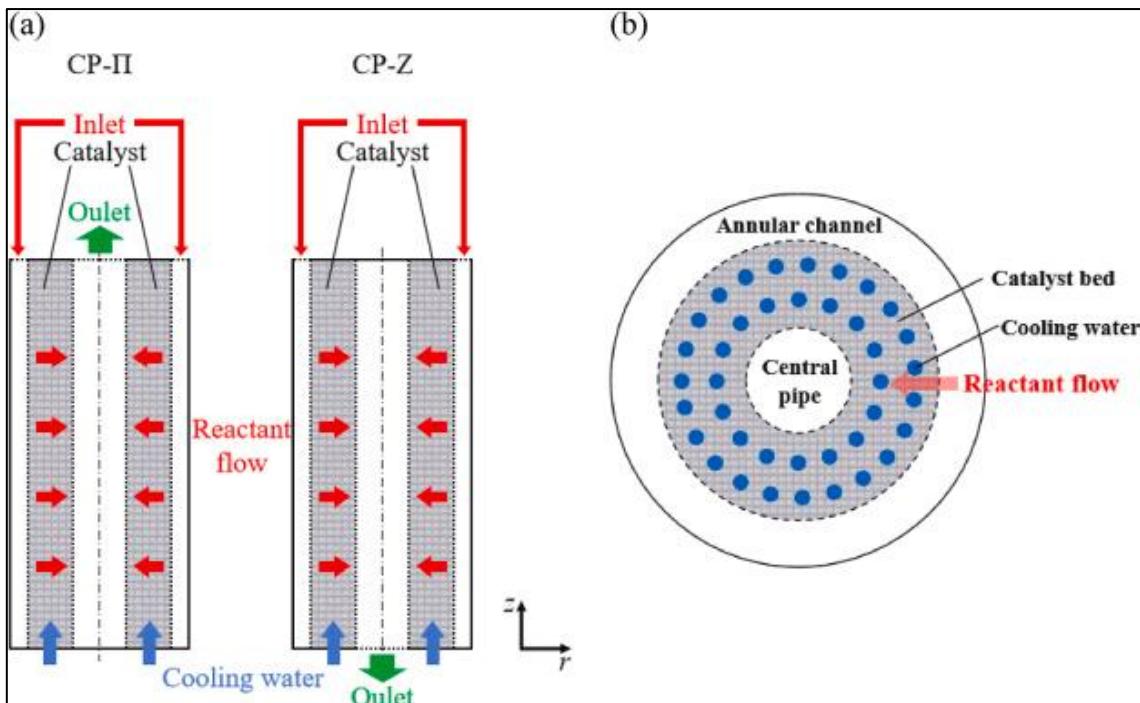
Radial Bed Reactors

- Radial-bed reactors represent one of the most significant engineering optimizations in ammonia synthesis technology.

- Their geometry, hydrodynamics, and thermal characteristics provide major advantages over traditional axial-flow packed beds, especially under high-pressure exothermic reaction conditions such as the Haber–Bosch process.



Radial Bed Reactor



Geometry and Flow Arrangement

- A radial-bed reactor consists of:
 - An outer perforated cylindrical wall.
 - An inner perforated cylindrical core.
 - A toroidal (annular) catalyst bed filling the space in-between.
 - Gas enters either:
 - From the outer wall → flows radially inward → exits through inner core
- OR**
- From the inner core → flows outward → exits at the outer wall.
 - Topsoe prefers: **Outer to Inner (i.e. Radially inward flow).**
- The Topsoe design typically uses radially inward flow, which promotes:
 - Lower gas velocities,
 - Minimal channeling,
 - Uniform pressure distribution.

- The surface area through which fluid flows is: $A_{flow}(r) = 2\pi r H$
- As radius increases, flow area increases, causing:
 - Lower velocity, $v \propto 1/r$
 - Lower pressure drop
 - More uniform distribution.

- **Hydrodynamic Advantages**

- As the flow cross-section expands radially, pressure drop is dramatically reduced compared to axial beds.
- Pressure drop comparison:

Reactor Type	Typical ΔP per meter
Axial bed	30–50 kPa/m
Radial bed	15–25 kPa/m

Table: Pressure drop comparison

- This happens because: $\Delta P \propto v^2$ and radial geometry naturally decreases velocity.
- The hydrodynamic stability eliminates:
 - Channeling
 - Hot-spot formation
 - Maldistribution problems (common in large axial beds).
- It benefits the process by:
 - Providing better RTD
 - Lower compressor/blower reactor
- **Heat Management in Radial Beds**
 - Ammonia synthesis is highly exothermic. Poor temperature control causes:

- Catalyst sintering
 - Thermodynamic penalties
 - Reduced Reaction Rate
- Radial Flow improves thermal control via:
 - **High Heat Transfer Coefficient**
 - The radial orientation increases:
 - Surface renewal rates
 - Boundary-layer thinning
 - Contact between gas and catalyst surface.
 - This yields a **20-40% increase** in effective heat transfer in axial beds.
 - **Internal Heat Exchangers**
 - Topsoe reactors incorporate **tube-bundle** H.E. between catalyst beds:
 - Hot effluent incoming cold gas
 - Each bed begins at a controlled temperature
 - Controls hot-spot magnitude.

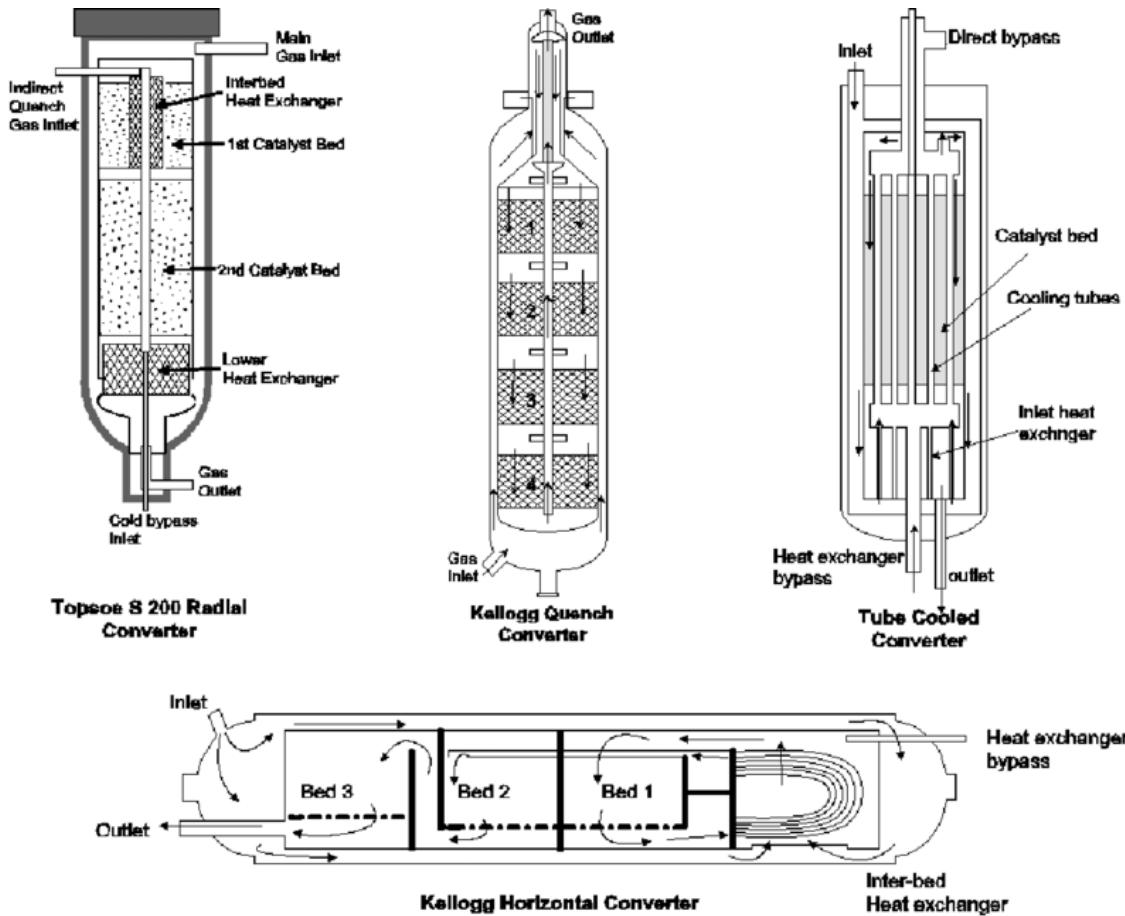


Fig.: In-Built Heat Exchangers in Radial Bed

- **Catalyst Utilization in Radial Beds**

- Radial flow ensures:
 - More uniform contact with catalyst
 - More consistent residence time distribution (RTD)
 - Better utilization of active surface area.
- Fewer stagnant zones → fewer inactive catalyst pockets → higher effective catalyst efficiency.
- Lower ΔP allows:
 - Smaller blower/compressor loads
 - Higher throughout for same catalyst mass

- **Mathematical Model - RFR**

- Unlike axial PFRs, radial reactors require **2D** modeling (radial + axial), but for thin beds, axial gradients are small and a 1D radial approximation suffices.

- **Radial Mass Balance**

- For radial flow:

$$\frac{dF_i}{dr} = 2\pi r H r_i$$

- Conversion formulation:

$$\frac{dX}{dr} = \frac{2\pi r H \eta r_{NH_3}}{F_{N_2,0}(1 + \varepsilon X)}$$

- **Radial Pressure Drop**

- Modified **Ergun Equation** (radial coordinates):

$$\frac{dP}{dr} = - \left[\frac{150(1 - \varepsilon)\mu v}{\varepsilon^3 d_p^2} + \frac{1.75(1 - \varepsilon)\rho v^2}{\varepsilon^3 d_p} \right]$$

- Radial Velocity:

$$v(r) = \frac{F}{2\pi r H}$$

- As r increases, v decreases, reducing the pressure drop sharply.

- **Temperature Profile**

- Radial conduction + convection:

$$\rho C_p v(r) \frac{dT}{dr} = k_{\text{eff}} \frac{d^2 T}{dr^2} + (-\Delta H_r) \eta r_{NH_3}$$

- In practice:

- Convective term dominates

- Temperature rises quickly at bed entry
- Inter-bed coolers reset the temperature
- Thus, radial reactors achieve:
 - Smaller hot-spot magnitude
 - Lower wall temperatures
 - Better catalyst preservation
- **Industrial Performance Outcomes**
 - **Conversion Efficiency**
 - Typical multi-bed Topsoe reactor:
 - **Bed 1:** 0 → 10–12%
 - **Bed 2:** 10 → 18%
 - **Bed 3:** 18 → 26–30%
 - **Catalyst Life**
 - Lower peak temperatures - slower sintering
 - Typical Catalyst Life:
 - **3 - 5 years**, with minimal annual deactivation (0.5-2%).
 - **Energy Efficiency**
 - Internal heat recovery improves thermal efficiency to:
 - **75-85%** total energy utilization.
- **Merits of Radial over Axial Reactors**

Metric	Axial Bed	Radial Bed
Pressure drop	High	Low
Flow distribution	Moderate	Excellent

Hot-spot risk	Higher	Lower
Catalyst utilization	Moderate	High
Efficiency	~80%	85–92%
Industrial preference	Rare in modern plants	Standard choice

Table: Merits of Radial over Axial Bed Reactors

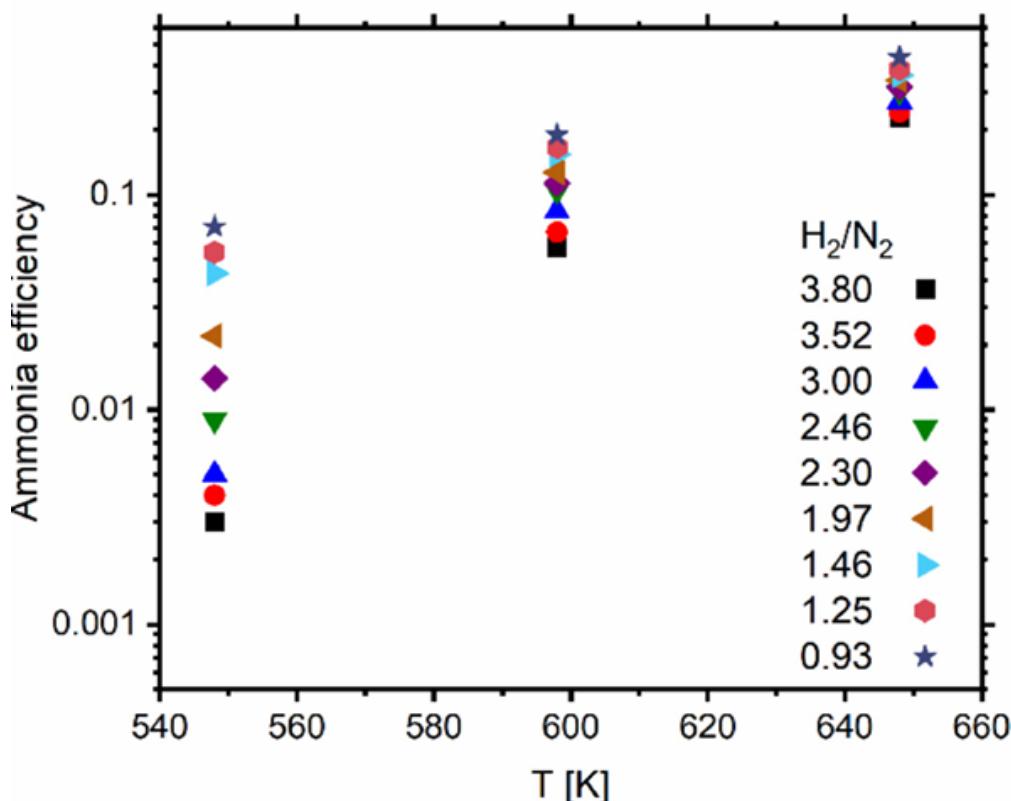
5. Insights from Paper:

Ammonia synthesis, though well established industrially, is still kinetically limited under practical pressures and temperatures. The recent work of Nadiri et al. (2024) revisited this problem experimentally and developed a new kinetic framework, the Extended Stoltze Model, that more accurately predicts ammonia formation across a wide operating range of temperature, pressure, and H₂, N₂ ratios.

Key Experimental and Modelling Insights

- **Operating ranges tested:**
 - Temperature **T = 598 – 748 K**
 - Pressure **P = 90 bar**
 - Feed ratios **H₂ : N₂ = 0.93 – 3.8**
- **Classical industrial conditions** were typically **3:1 H₂ : N₂; 100 bar; 573 – 673K** with empirical reaction orders = 0.5 – 0.75.
- **Extended investigations** showed that the apparent order and rate vary significantly with composition, validating the need for a variable site-density model.
- The **lowest ammonia yield** occurs at the **highest hydrogen ratio**, even though equilibrium would predict the opposite. This inversion arises because excess hydrogen poisons the catalyst surface. Hydrogen atoms occupy the active iron sites that would otherwise dissociate N₂.

- At low temperature, increasing partial pressure of H₂ has a negative effect on synthesis rate (strong adsorption, slow N₂ activation), whereas at higher temperatures (> 700 K) the hydrogen inhibition weakens and the rate increases.
- The active-site density μ_s grows almost linearly with temperature, indicating greater catalyst availability as chemisorbed species desorb.
- Reported kinetic fits covered hydrogen-to-nitrogen ratios from ≈ 1:1 to 6:1 and confirmed that the reaction order with respect to each reactant stays in the 0.5 – 0.75 range.



Integration with MATLAB Simulation

In our work on the **Topsoe Ammonia Process**, these observations were embedded into the MATLAB model through:

- **Equilibrium yield estimation** using Shomate-based thermodynamics:

$$K_p(T) = \exp[-\Delta G^\circ(T)/(RT)]$$

provided the theoretical limit $y_{NH_3, eq}$.

- **Efficiency evaluation:**

$$\eta = y_{out}/y_{eq}$$

- Quantified how closely the process approached equilibrium.
- **Variable feed composition:** We simulated **H₂:N₂ = 0.7, 0.75, 0.8** (2.3 – 4.0 ratio range) at **698 K** and **90 bar**.

The equilibrium mole fractions obtained were:

Case	T_K	P_bar	H2_frac	N2_frac	y_NH3_out	y_NH3_eq	xi	eta
1	598	90	0.75	0.25	0.0365	0.002004008	0	18.214
2	648	90	0.75	0.25	0.0775	0.002004008	0	38.673
3	673	90	0.75	0.25	0.0949	0.002004008	0	47.355
4	698	90	0.75	0.25	0.1097	0.002004008	0	54.74
5	773	90	0.75	0.25	0.0997	0.002004008	0	49.75

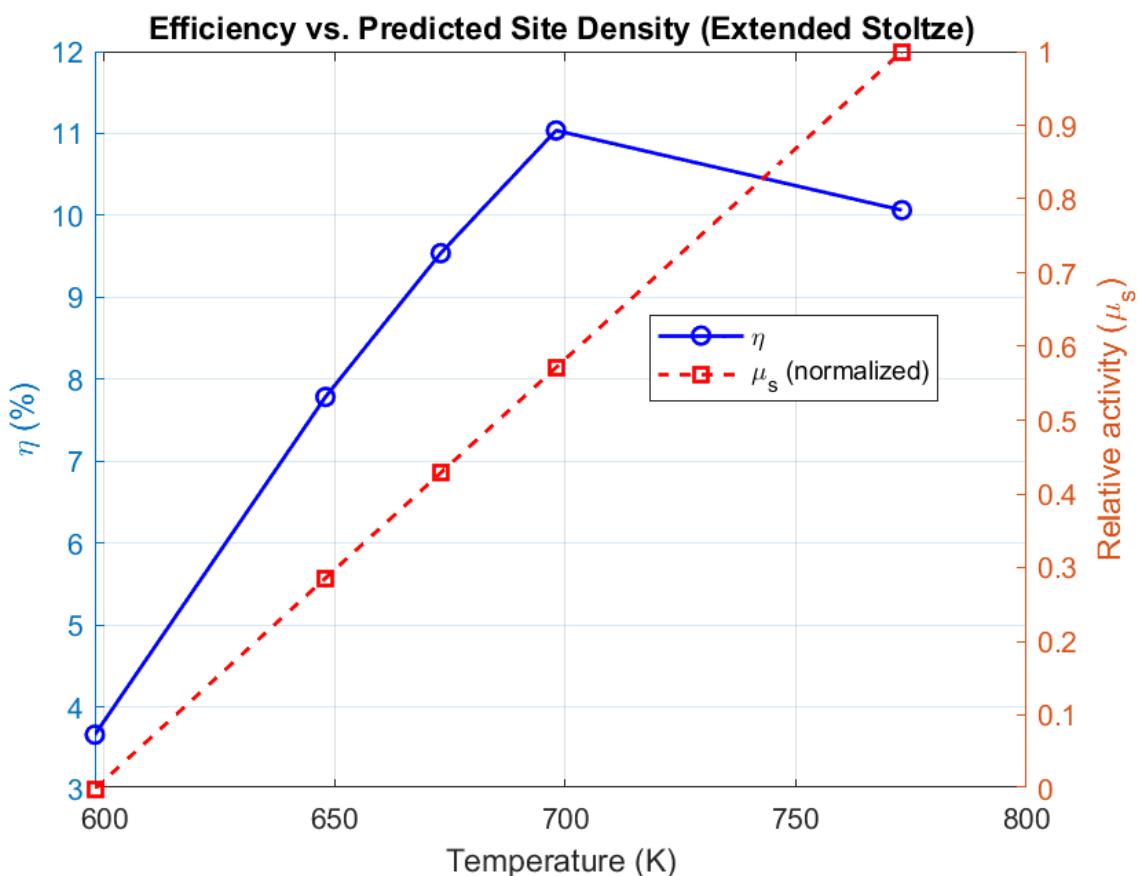
showing a modest increase in equilibrium yield with more hydrogen but confirming that, under real catalytic operation, efficiency drops at very high H₂ ratios, matching Nadiri et al.'s trend.

- **Extended Stoltze active-site correlation:**

$$\mu_s = 1.91 \cdot (T - 618) - 1.52 \cdot (p_{H2} - 46.25) + 78.61$$

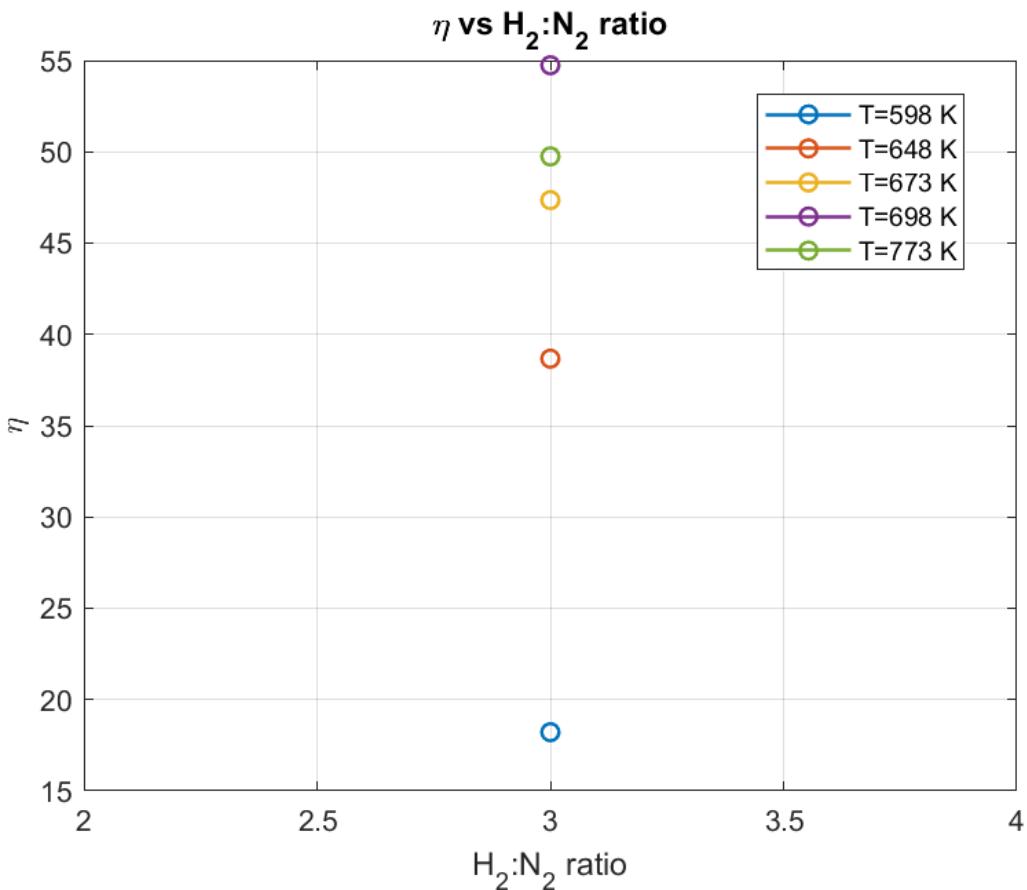
was implemented to compute temperature- and pressure-dependent catalyst activity.

The combined plot of **η vs. μ_s** demonstrated that efficiency follows the same temperature dependence as predicted site density, validating that our reactor's performance is governed by active-site availability.



Comparison and Interpretation

Temperature region	Controlling factor	Behaviour in MATLAB / Paper
550 – 620 K	Kinetic limitation	Low η , low μ_s , hydrogen-poisoned surface
650 – 700 K	Optimal range	Rapid rise of η with μ_s , best balance
> 700 K	Thermodynamic limitation	μ_s still increases but η slightly drops due to NH ₃ decomposition



Industrial Relevance

For **Topsoe's systems**, these correlations confirm:

- The process efficiency is dominated by catalyst surface dynamics, not just equilibrium thermodynamics.
- Flexible operation under fluctuating renewable-hydrogen feeds can be modelled by adjusting $\mu_s(T,pH_2)$ in real time.
- Maintaining moderate $H_2:N_2 \approx 3 - 3.5$ ensures maximal yield without surface poisoning—consistent with both literature data and Topsoe design practice.

Conclusion:

The MATLAB equilibrium and efficiency analysis, coupled with the Extended Stoltze site-density formulation from Nadiri et al. (2024), successfully reproduces the experimentally observed dependence of ammonia yield on temperature and $H_2:N_2$ ratio. At 698 K and 90 bar, the predicted efficiency increases with temperature and correlates

closely with calculated μ_s , confirming that catalytic site availability drives reactor performance. The integrated model therefore bridges classical thermodynamics with modern kinetic insights, aligning the Topsoe process simulation with current academic understanding of flexible green-ammonia synthesis.

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The End...