TOPSOE AMMONIA PROCESS

Course: Applied Process Engineering - CH203G

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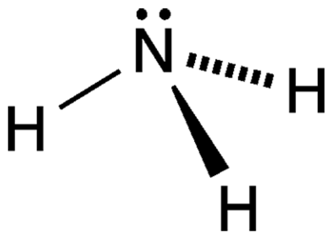
1. A. What is NH_3?



- Ammonia is a versatile chemical compound that has primarily been used as a fertilizer in agriculture to feed the world's growing population, as well as in the production of numerous other chemicals, such as plastics, pharmaceuticals, and explosives.
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- Ammonia, as a low-carbon energy carrier, is receiving significant attention. Its high-energy density makes it an attractive fuel source, and when produced through a sustainable production method (low-carbon or green ammonia), ammonia is considered a game changer in decarbonizing the maritime industry and other energy-intensive industries where direct electrification is not an option. This will create a need for larger-than-ever-built capacities.
-
- Being easy to store and transport, ammonia can be distributed worldwide by means of trucks, trains, ships, and pipelines. Ammonia is often discussed as the energy carrier and storage medium of the future and is considered an important transportation method for hydrogen.
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- With the Haber-Bosch Process being one of the first to start the industrial production of ammonia, there have been significant advances in the field of ammonia production. One such advanced process/producer of ammonia is the **Topsoe Process.**

1.B.a. History:

"Dr. Haldor Topsøe founded the company in 1940 (Denmark), based on two things: A passion for science and a determination to make a positive difference in the world.**"**

- When growing up as a young man in the 1920s and 1930s, Dr. Haldor Topsøe saw many challenges. As a young scientist, he felt he needed to do something. Because he could. This led him to establish the company Haldor Topsøe.

1. Introduction:

- Dr. Haldor Topsøe’s **interest in chemistry and catalysis** was sparked during his study of physics with the prominent professor, **Niels Bohr**, at the Niels Bohr Institute in Copenhagen. That is where Dr. Haldor Topsøe first saw the potential of catalysis, which would become the basis of the company.
- Though catalysis was not prominent back then, Dr. Topsoe believed that one day it could serve a huge, unmet industrial need.
- Topsoe’s ammonia solutions have supported **fertilizer production** that has secured food for growing populations.
- Already in 1988, Dr. Haldor Topsøe predicted the climate challenges faced today:

“I wish you would understand that the greenhouse effect will reach a point of no return, but we can postpone this through a more efficient use of fossil fuels and continued expansion of renewable energy.**”**

- Dr. Haldor Topsøe’s contributions were recognized with many honors. These included the **Eminent Chemical Engineer Award** in Delhi in 1997. In 1999, he was awarded the **Engineer of the century** in Denmark for his devotion to chemical engineering and his determination to make science serve humanity and our planet.

1.B.b. Infrastructure:

1) Raw Materials:
   - **Natural Gas** – It serves as the primary feedstock. It provides the necessary Hydrogen needed for the process
   - **Water** – It is an important raw material, as it is used to produce syn gas
   - **Air -** It provides the necessary N_2 required for the process.
   - **Catalysts -** The process uses Fe and Ni – based catalyst, typically used for reforming, and synthesis processes to enhance reaction rates and efficiency.
2) Storage of Raw Materials:
   - **Natural Gas Storage –** They are often stored in facilities with pressurized tanks, or underground tanks.
   - **Water Storage –** Tanks are utilized for demineralized or treated water.
   - **Syn Gas Storage –** Syn gas is stored in temporary containers, produced during reforming.
   - **Liquid Ammonia Tanks –** Large, insulated tanks to store ammonia, typically under pressure to keep it in liquid form. Areas to facilitate tanks, trucks, and other transportation.
3) Geographical Conditions of the Storage Location:
   - **Climate –** Oceanic climate/temperature is preferred.
   - **Location –** Headquartered at Denmark. It has branches in various countries, including India. (Combination of favorable climate conditions, and strategic global presence are considered).
4) Reaction Conditions:
   - **Temperature** – Different equipment is kept at a different temperature, typically ranging from 200 – 1000 °C.
   - **Pressure –** Similarly, the process is carried out at high pressures, typically at either 20-30 bar or 150-200 bar.

1.B.c. Types of Ammonia Produced:

Topsoe produces ammonia in 3 methods:

- Green Ammonia:
  - It is projected for green ammonia to account for two-thirds of the total ammonia production by 2050.
  - It is produced from green hydrogen and nitrogen.
  - Uses S-300 Converter and KM1 catalyst.
- Blue Ammonia [Low-Carbon Ammonia]:
  - Blue ammonia is a responsible way of producing ammonia that integrates carbon capture to minimize GHG emissions
  - It is projected to have an increase of 688 MT in production and a market value of 400 billion by 2050.
  - It uses SynCOR™ Ammonia technology.
- Grey Ammonia [Conventional Ammonia]:
  - It uses SynCOR Ammonia technology.

2. Salient Features:

2.A. Advanced Catalyst Tech:

- Their proprietary catalyst technology ensures a high conversion rate for ammonia production, from raw materials. These catalysts withstand elevated temperature and pressure, ensuring lifespan, and reducing costs.
- Ni and Fe based catalysts are prominently used.

2.B. Integrated Production:

- Topsoe has an integrated Hydrogen production system, through SMR or other methods.
- This provides a steady supply of high-purity Hydrogen.

2.C. Modular Design Plant:

- It provides modular plants for easy scaling.
- ModuLite™ Green Ammonia Plant makes this possible and is available in 300 and 600 MTPDversions.

2.D. Heat Recovery System:

- It uses advanced heat recovery systems to reuse waste energy/heat. This increases plantefficiency, as input energy is less.

2.E. Technology and procedures:

- It works on the principle of recycling ($CO2$ or heat or others), increasing efficiency.
- It also uses advanced technology ensuring safety and efficiency of production.
- S – 300 Converter**:**
    - The converter's three catalyst beds with radial flow allow for higher conversion ratesusing small catalyst particles. This results in higher overall catalyst activity, meaninggreater overall efficiency and higher profit margins.
    - Advantages for green ammonia production include the ability to ramp up and down withfluctuating feedstock loads, as well as sustained reliable operation at loads down to 10%of nameplate capacity.
- SynCOR Ammonia Technology**:**
    - The technology brings significant benefits in large-scale applications, most notably anextremely low steam-to-carbon ratio of 0.6 and potential for single-train capacities

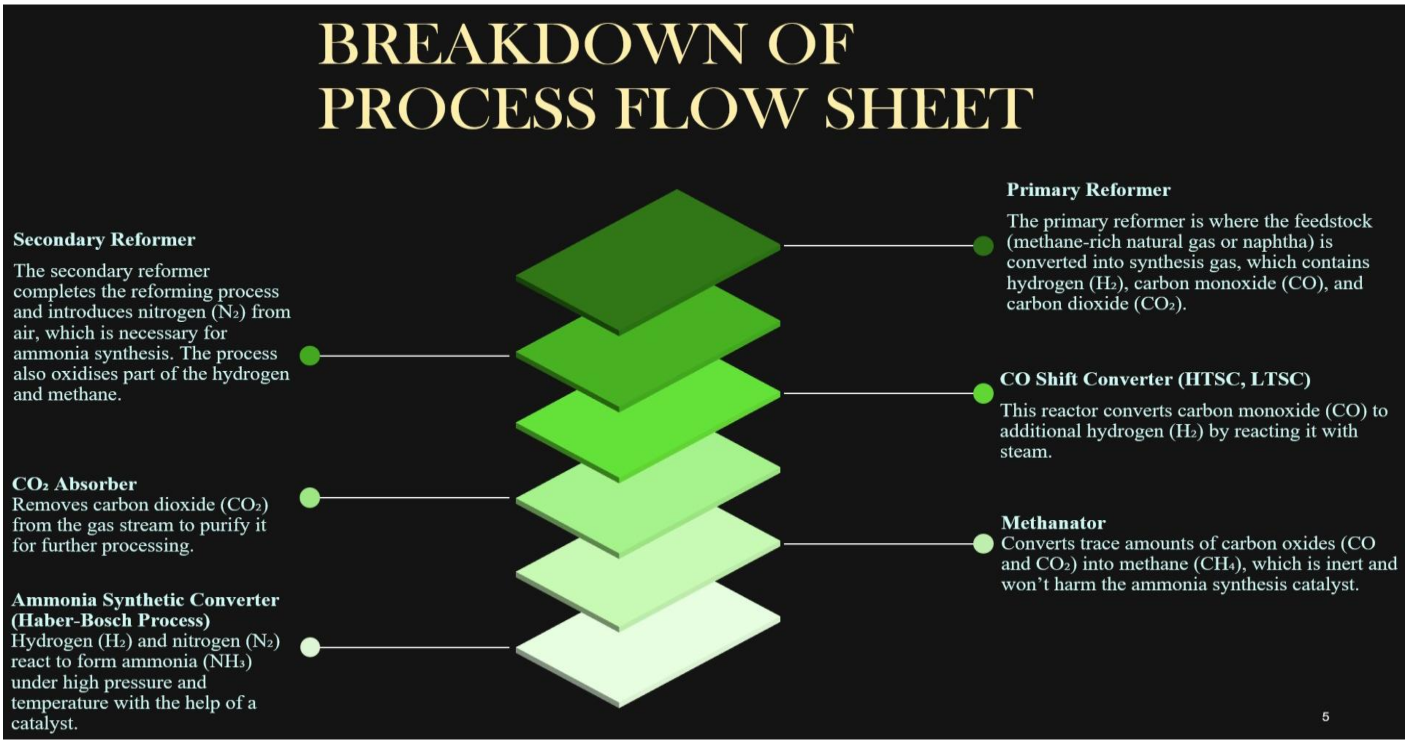
exceeding 6,000 MTPD. This enables ammonia and urea producers to gain unprecedented economies of scale that cannot be achieved with conventional technology.

- Some advantages:
  - Low steam-to-carbon ratio
  - Exceptionally low water consumption
  - Reduced environmental impact
  - Great economy of scale
  - High safety
  - Technology for generous size plants

- With Catalyst:
  - Maximize plant's design efficiency and sustain its performance
  - Minimize supply-chain risks with catalysts developed using non-exotic materials
  - Enjoy comprehensive support based on out of eight decades of ammonia-industryexperience.

  - KM1 - Promoters that ensure high and stable activity.
    - Advantages:
      - Long-term reliability
      - Superior and stable activity
      - Outstanding poison resistance
      - Pre-reduced option for fast startup

3. What happens in the Process?



3.1. Preheater

- NAPHTHA is taken as feed, along with FG, and is heated to a certain desired temperature. The temperature range is typically ~ 800 – 950 °C.
- Calculating ΔH :
- Calculated by finding the Cp value for methane from Perry's handbook.
- Solved using the below MATLAB code.

MATLAB CODE:

```
% dH = Cp*dT
% Cp = 5.34 + 0.0115*T

dH = @(T) 5.34 + 0.0115*T;

% Initial & final temperature
T1 = 373;
T2 = 623;

result = integral(dH, T1, T2);
del_H_joule = result*4.184;     % del H is 11576.08 J/mole
```

3.2. Desulphurization

- Hydrogenator:
    - Naphtha containing impurities like sulphur, when processed in a hydrogenation unit,reacts with hydrogen to produce alkanes and H S.
    - During this process, the sulphur impurities are removed as H S gas, while the unsaturated hydrocarbons in naphtha areconverted to alkanes.

$R\text{-}S + H_2 \rightarrow R\text{-}H + H_2S$

- H_2S Absorber:
    - When the mixture of alkanes and H_2S is fed into an H_2S absorber, the absorber selectively removes the H_2S from the mixture, leaving behind only alkanes.
    - Typically,the absorber contains a solvent or chemical agent, such as an amine solution, that reacts with or absorbs the H_2S, resulting in purified alkanes in the output stream.
- Adiabatic Reformer:
    - When alkanes are fed into an adiabatic reformer, they undergo a steam reforming reaction with water (steam), producing CO and H_2 as the primary products.
    - This reaction typically occurs at elevated temperatures and is endothermic, but in an adiabatic reformer, no external heat is supplied, so the reaction relies on the heatgenerated from the previous reactors.

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)\,H_2$$

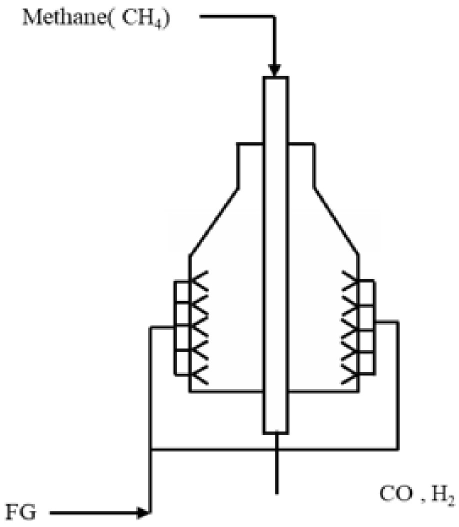
3.3. 1^0 Reformer

- The primary reformer is where the feedstock (CH_4-rich natural gas or naphtha) is converted into synthesis gas, which contains H_2, CO_2, and CO.

- Inputs**:**
    - **Hydrocarbon feedstock:** Natural gas (CH_4) or NAPHTHA (complex hydrocarbons)
    - **FG:** High-pressure steam is added for the steam reforming reaction.
    - **Catalyst:** Typically, a nickel-based catalyst is used to facilitate the reforming reaction

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

- Calculating the unknows:
- Unknowns: m_2, x_1, x_2, x_3
- Calculating the unknowns using mass and atomic balance.




```
m1 = 90277.78;
mS1 = 128472.22;
m2 = m1 + mS1 % Total balance

eff = 0.95; % Efficiency
x1 = (1-eff)*m1/(m2)  % Fraction of conversion
% O & C balance equations
A=[2*m2 m2; m2 m2] ;
B=[mS1; m1-(x1*m2)];
A1=inv(A) ;
X=A1*B;
x2=X(1,1)
x3=X(2,1)
```

- Output:

```
m2 =

     218750


x1 =

    0.0206


x2 =

    0.1952
```

x3 =

0.1968

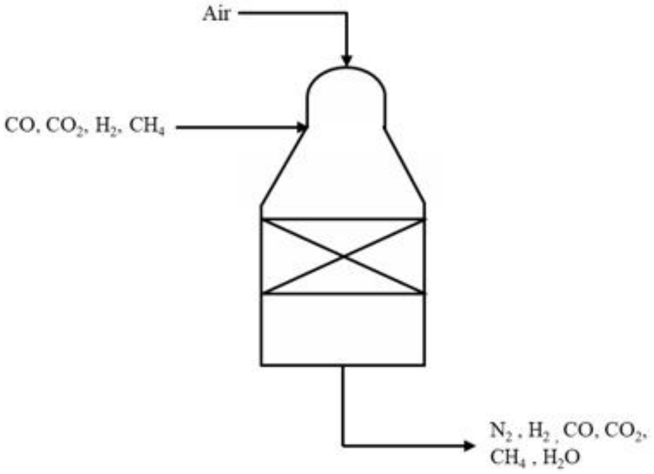
- Outputs**:**
    - **H_2 :** Main component needed for ammonia synthesis.
    - **CO:** A byproduct that will be converted into a 2° reformer or later processed.
    - **CO_2 :** Produced in small quantities.
    - **CH_4 :** A portion of methane remains unreacted.

3.4. 2^o Reformer

- The secondary reformer completes the reforming process and introduces N_2 from the air, which isnecessary for ammonia synthesis. The process also oxidizes parts of H_2 and CH_4.
- Inputs**:**
    - **Output gas from the primary reformer:** Contains H_2 , CO, CO_2, and unreacted CH_4.
    - **Air:** Provides N_2 and O_2.
    - **Catalyst:** Ni-based or other reforming catalysts.

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \text{ (exothermic)}$$
$$H_2 + 0.5O_2 \rightarrow H_2O \text{ (exothermic)}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ (endothermic)}$$

- Values after solving:
- $X_2 = 0.0696$
- $X_3 = 0.0405$
- $X_5 = 0.1865$
- $X_6 = 0.5348$
- **Outputs**:
    - **H_2 :** In larger quantities.
    - **N_2 :** Introduced from the air, needed for ammonia synthesis.
    - **CO:** Residual amounts.
    - **CO_2:** Increases due to reforming and partial combustion.
    - **H_2O:** Produced from combustion.
    - **CH_4 :** Trace amounts remain unreacted.



3.5. CO Shift Converters

These reactors convert CO to additional hydrogen H_2 by reacting it with steam.

- Inputs:
  - **Syn gas** from the secondary reformer: Contains CO, H_2 , CO_2, and H_2O (g).
  - **H_2O (g):** Used in the water-gas shift reaction.
  - **Catalyst**: Typically, iron-based or copper-based catalyst.
- Reaction:
  - Water-Gas Shift Reaction:

$$\boxed{CO + H2O \rightarrow CO2 + H2}$$

- Outputs:
  - **H_2:** More hydrogen is produced.
  - **CO_2:** Byproduct of the shift reaction.
  - **Residual CO:** Exceedingly less amounts remain.
  - **H_2O:** Present as vapour or liquid, depending on the system.

3.5.1. HTSC:

- High Temperature Shift Converter operates at high temperature.

MATLAB CODE:

```
% Define Cp functions for CO and CO2
Cp_CO = @(T) 6.6 + 0.0012*T;
Cp_CO2 = @(T) 10.34 + 0.00274*T - (195500 ./ (T.^2));  % Use element-wise division

% Initial & final temperature
T1 = 573;
T2 = 673;


delta_H_CO = integral(Cp_CO, T1, T2);
```

delta_H_CO2 = integral(Cp_CO2, T1, T2);

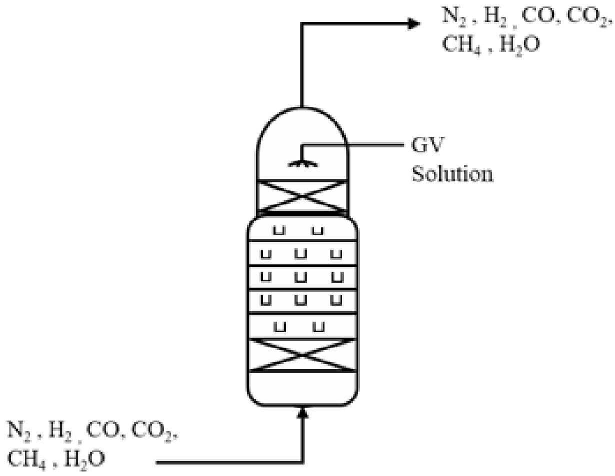
delta_H_reaction = delta_H_CO2 - delta_H_CO; % del H is 419.2456 J/mole

3.5.2. LTSC:

- Low Temperature Shift Converter operates at low temperature.
- They convert CO to CO_2.
- This ensures that the reactions occur without CO_2 interference.

3.6. CO_2 Absorber:

- Removes CO_2 from the gas stream to purify it for further processing.
- Input:
  - **Shifted Synthesis Gas:** Contains H_2, CO_2, CO, N_2.
  - **Solvent/Absorbent**: A chemical like monoethanolamide (MEA) or potassium carbonate is used to absorb CO_2**.**
- Reactions:
  - **CO_2 Absorption:** CO_2 is captured, creating CO_2 free environment.
- Output:
  - **H_2 and N_2:** Ready for further reactions.
  - **Absorbed CO_2:** Collected by solvent and stripped for recycling or other use.



3.7. Methanator:

- Converts trace amounts of carbon oxides (CO and CO_2) into methane (CH_4), which is inert and will not harm the ammonia synthesis catalysts.
- **Input:**
  - **CO – removed synthesis gas**
  - **H_2 gas**
  - **Ni-based Catalyst**
- **Reactions:**

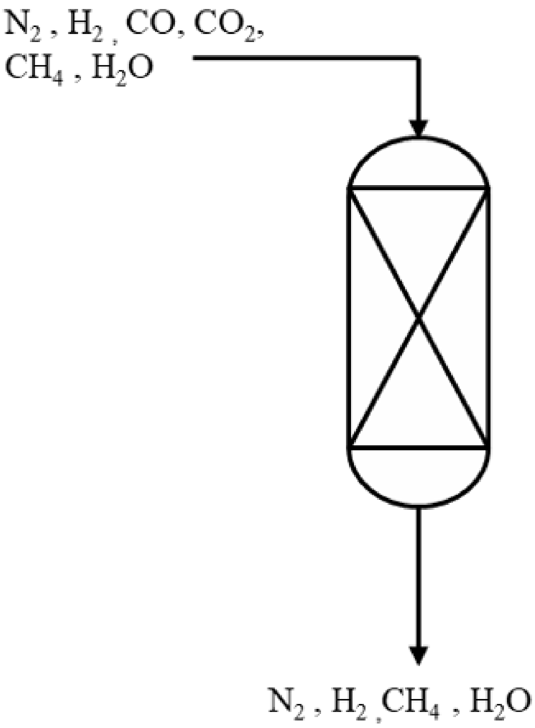
- **CO Methanation**:

CO Methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$ (exothermic)

- **CO Methanation**:

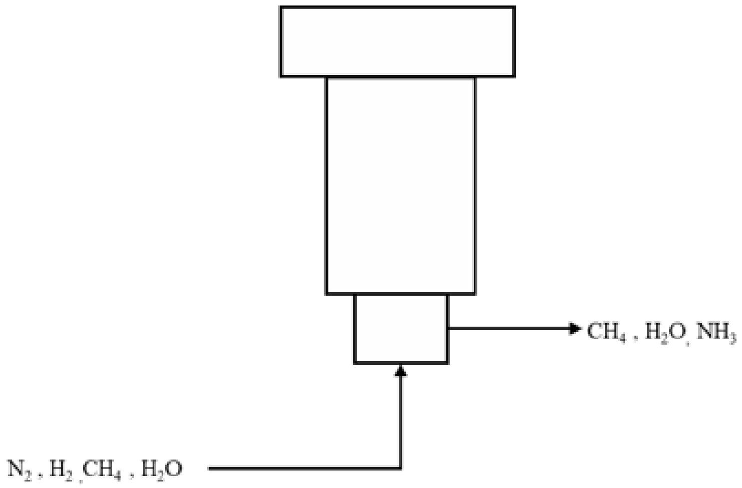
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (exothermic)

- **Output:**
  - **Inert CH_4 gas**
  - H_2O
  - H_2 and N_2



3.8. Ammonia Synthesis Converter:

- H_2 and N_2 react at high temperature and Pressure with Iron-based Catalyst.
- Input:
  - H_2
  - N_2
  - Iron-based catalyst
- Reaction:
  - Haber-Bosch Process: **$N_2 + 3H_2 \rightarrow 2NH_3$**
- Output:
  - Ammonia
  - Unreacted H2 and N2.



4. Course concepts and techniques used:

4.A. Chemical Process Calculations:

- Material balance
- Energy balance
- Flow Diagrams
- The overall working of the Processes can be studied using CPC concepts, as it lays the foundation for the process calculation.

4.B. Computational techniques for Chemical engineers:

- Solving linear equations using MATLAB
- Solving integrals using MATLAB
- Simulation, calculation and visualization of processes can be carried out and performed using numerical methods and software like MATLAB.

4.C. Fluid and Particle Mechanics:

- Data of head losses in the equipment:

• Pipe Material	Use section	Typical Diameter (m)	Length (m)	Velocity (m/s)	Friction factor (f)	Head loss (m)	Energy Loss (J/kg)
Carbon Steel	Feedstock, Low – temp pipes	0.2	100	3	0.018	0.82	8.0
Stainless steel	CO_2 rich	0.15	100	5	0.015	2.55	25.0

High Alloy steel	Reformer temp outlet	0.3	100	10	0.012	1.63	16.0
Low Alloy steel	High-pressure synthetic gas	0.1	100	20	0.020	8.12	80.0
Ferritic stainless steel	HTSC and LTSC gas pipes	0.15	100	8	0.017	3.47	34.0

4.D. Process Heat Transfer:

- Energy balance
- Heat losses
- Heat exchangers
- Temperature maintenance of reactors and converters.

4.E. Thermodynamics:

- Energy balance
- Heat recovery
- Waste recycling (Heat and Material)

5. Comparison

- A detailed comparison between different ammonia synthesis process.

Process	Catalyst	Energy Consumption (GJ/t)	Energy Loss (%)	Energy Produced (GJ/t)	Shutdown Time (days/year)	Total Energy (GJ/t)	Feedstock Type	By-products
Topsoe	Iron-based	~7-10	20	1.5	~15-20	9.0	Natural gas, air	Hydrogen, nitrogen
Haber-Bosch	Iron-based ($Fe2O3$)	~7-10	25	2.0	~20-30	10.5	Natural gas, air	Trace gases, heat
Linde	Ruthenium (Ru)	~6-9	12	2.5	~10-15	8.5	Natural gas, air	Minimal
Krupp Uhde	Iron or Ruthenium	~6.8-9	17	2.0	~15-25	9.0	Natural gas, air	Minimal
KBR	Iron-based	~7.2-9	22	2.0	~20-25	9.5	Natural gas, air	Trace gases, water

6. Pros of Topsoe:

- **Lower Pressure Operation:**
  - The Topsoe process operates at relatively **moderate pressures (50-100 bars)** compared to the **Haber-Bosch process (60-180 bars)** and **Linde process (150-300 bars)**. This reduces the need for high-pressure equipment, improving **safety** and **reducing operational costs**.
- **Moderate Temperature:**
  - The Topsoe process uses a **temperature range of 370-460°C**, which is lower than the **Krupp Uhde process** (740-950°C). Lower operating temperatures improve **catalyst life** and reduce the energy required for the process.
- **Iron-Based Catalyst:**
  - The **iron-based catalyst** used in the Topsoe process is **cost-effective** and readily available, compared to more expensive catalysts such as the **platinum-rhodium** used in Krupp Uhde.
- **Adaptability:**
  - The Topsoe process is adaptable and can be integrated with various hydrogen production methods, including **steam reforming, electrolysis, and natural gas**.
- **Efficient Use of By-products:**
  - By-products such as **CO , olefins, and aromatics** can be separated and used in other chemical processes, adding value to the production chain.

7. Cons of Topsoe:

- **Lower Daily Yield:**
  - The Topsoe process has a daily yield of **1,650 metric tons**, which is significantly lower than other processes like **Krupp Uhde (3,300 metric tons)** and **Haber-Bosch (>3,000 metric tons)**. This may limit the scalability of the process for large-scale ammonia production.
- **Higher Energy Consumption:**
  - The Topsoe process consumes **7.2 MWh per ton of ammonia**, which is higher compared to the **Linde process (0.4078 MWh/ton)** and even slightly higher than the **Krupp Uhde process**. This makes it less energy-efficient in comparison to the alternatives.
- **More Complex By-product Handling:**
  - The Topsoe process produces several by-products, including **CO , H S, olefins, and aromatics**. This requires additional separation and handling processes, increasing the complexity and cost of the plant's operations.
- **Shorter Maintenance Interval:**
  - The Topsoe process requires a shutdown every **32 days**, which is more frequent than the **Haber-Bosch process** (which typically runs for **1-3 years** between major shutdowns). This can lead to more frequent downtime and potentially higher maintenance costs.
- **Lower Process Flexibility:**
  - Compared to processes like **Linde** and **Krupp Uhde**, which can handle a wider range of feedstocks (such as natural gas and air), the Topsoe process primarily uses **pure H and N** , limiting its flexibility in terms of feedstock variability.

8. Nomenclature:

1. NH_3 – Ammonia
2. H_2 – Hydrogen
3. N_2 – Nitrogen
4. S – Sulphur
5. H_2S – Hydrogen Sulphide
6. CH_4 – Methane
7. H_2O – Water
8. CO – Carbon monoxide
9. CO_2 – Carbon Dioxide
10. Fe – Iron
11. Ni – Nickel
12. FG – Fuel Gas
13. GV – Gas absorbing solution
14. WHB – Waste Heat Boiler
15. BFW – Boiler Feed Water
16. Hot HE – Hot Heat Exchanger
17. HTSC – High Temperature Shift Converter
18. LTSC – Low Temperature Shift Converter
19. KM1 – a Catalyst
20. MT – Metric Tonne
21. MTPD – Metric Tonnes Per Day
22. Syn gas – Synthetic Gas
23. S-300 - A type of Reactor
24. SMR - Steam Methane Reforming
25. GHG – Greenhouse Gases
26. ™ - Trademark symbol

9. References:

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