

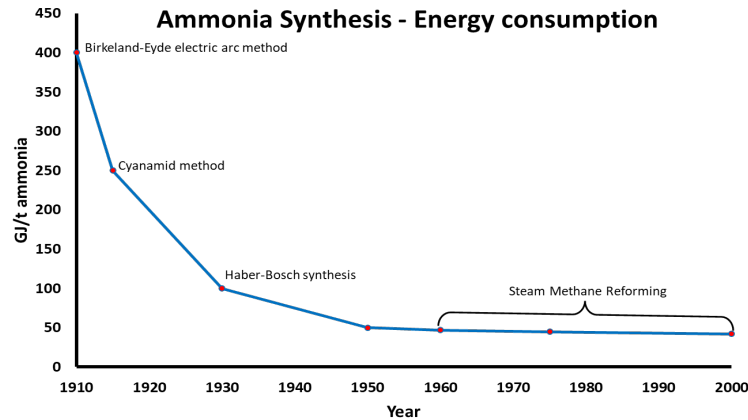
Decarbonizing Ammonia Production via Biomass-based Chemical Looping integrated Ammonia Synthesis

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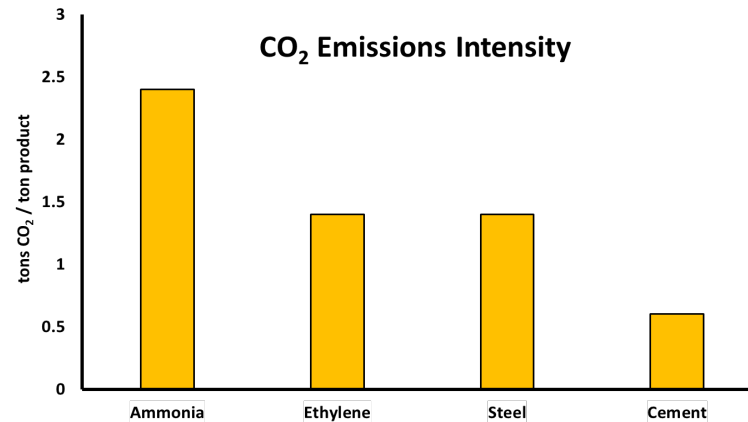
Motivation

Historical Development



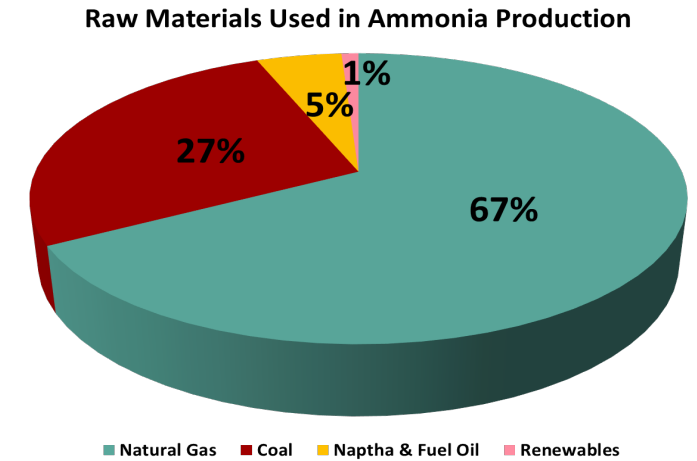
- Highly **energy-intensive** process.
- Significant improvement in the early 20th century, only **incremental improvement** in the last 50 years.

CO₂ Emissions



- **Highest CO₂ emissions intensity** among major commodity products.
- Source of emissions is high energy demand and production of reactants (H₂ and N₂).

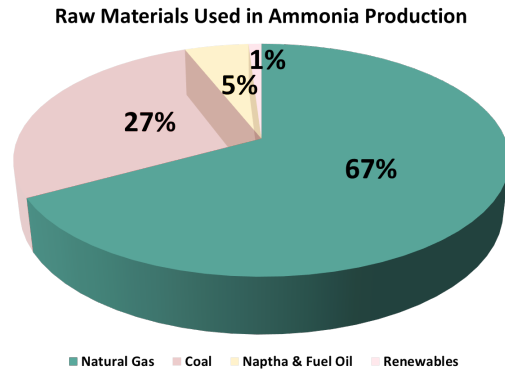
Raw Materials



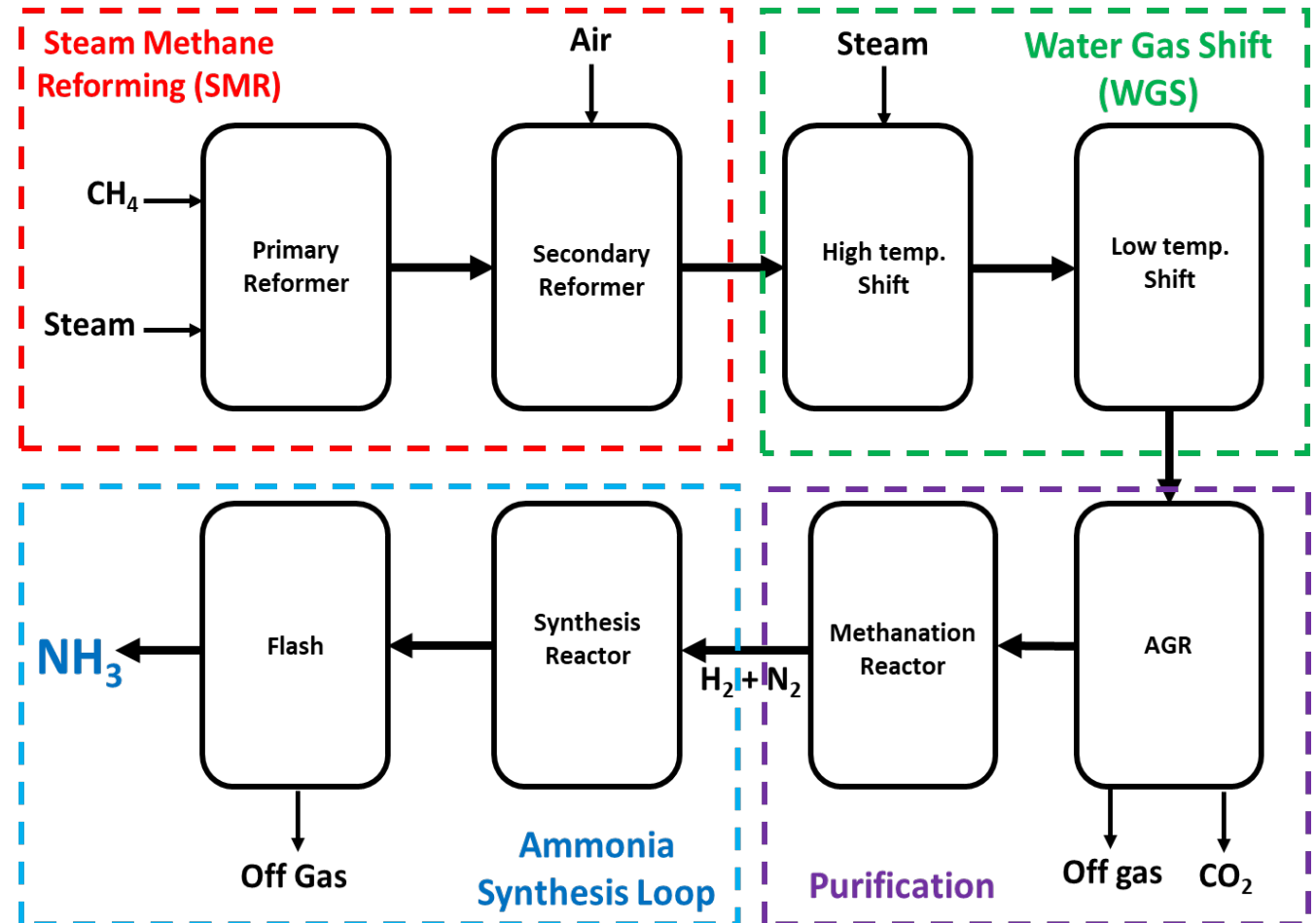
- **99% dominance** of fossil fuels for both meeting energy demand as well as reactants production.

Traditional Processes

Steam Methane Reforming (SMR)

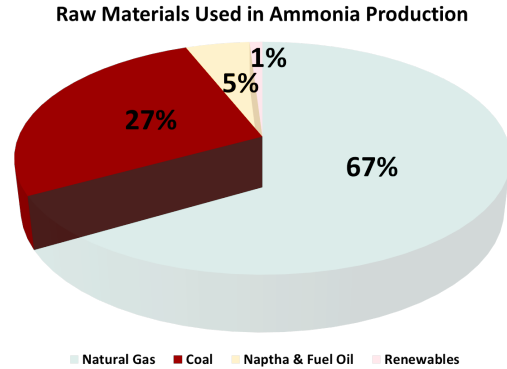


- Current state-of-the-art process.
- Requires more than **7 reactors** – involving dual reformer combination (SMR + ATR), WGS, AGR, and NH_3 synthesis loop.
- Uses **natural gas** as a feedstock.
- External heat input provided by burning natural gas, requiring an **additional CO_2 capture system**.

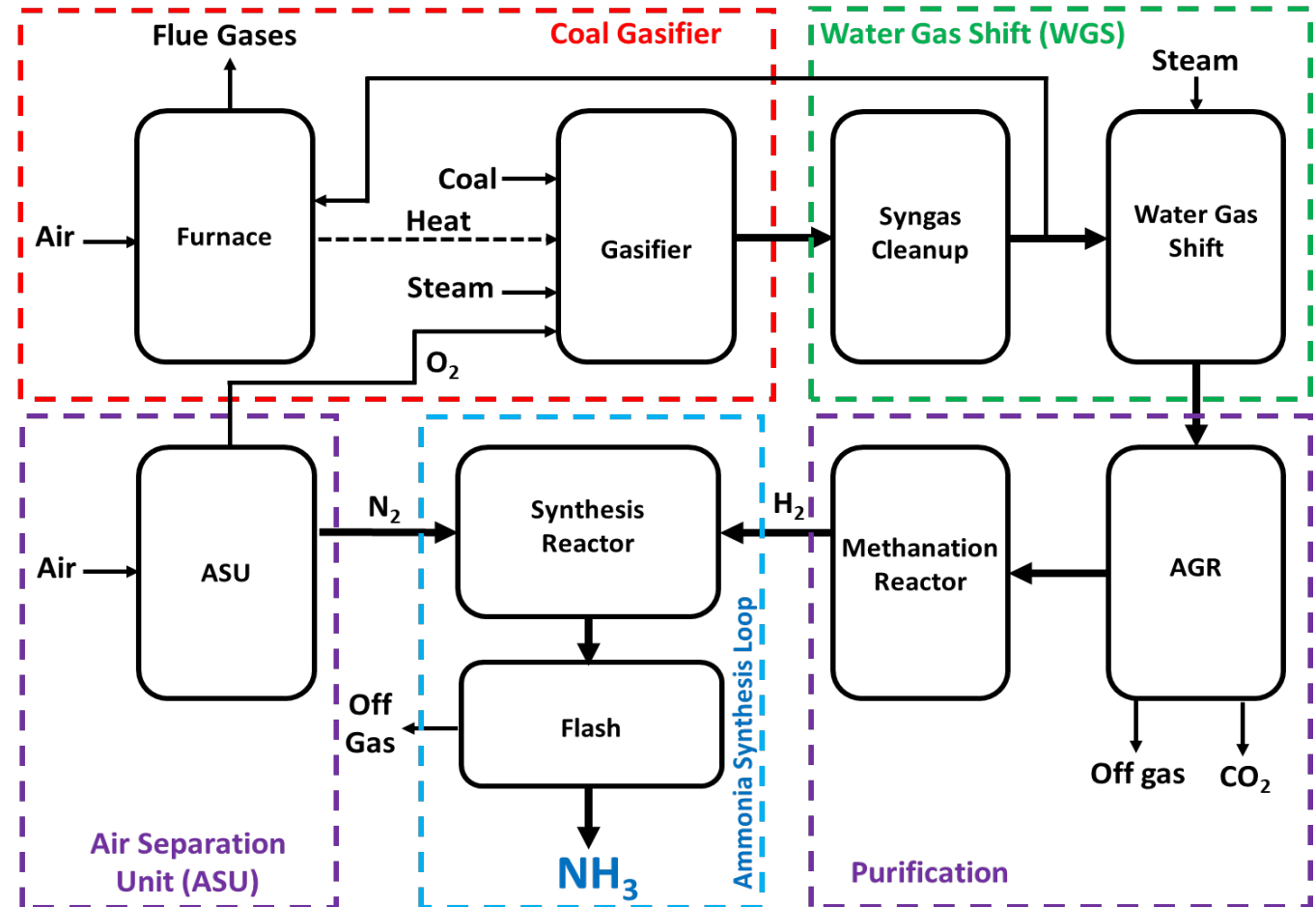


Traditional Processes

Coal Gasification



- Requires more than **8 reactors**: involving a gasifier, syngas cleanup, WGS, AGR, ASU, and NH_3 synthesis loop.
- Uses **coal** as a feedstock.
- External heat input provided by burning product syngas, requiring an **additional CO_2 capture system**.
- Use of ASU significantly increases energy demand and associated CO_2 emissions.



Decarbonization

Two approaches to decarbonization

Refine the Haber-Bosch process

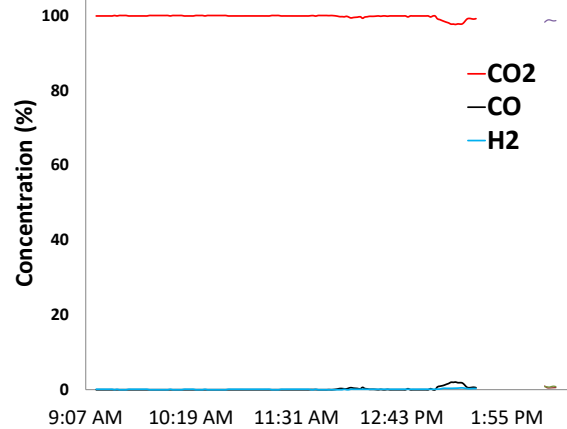
- Developing **better catalysts** with milder operating conditions and higher conversions.
- **Process Intensification** to reduce thermodynamic equilibrium penalties.
- Use of **renewable electricity for gas compression** and heating.
- Breakthrough alternative synthesis methods – **Electrochemical synthesis, photochemical synthesis, Metal-nitride chemical looping, biological synthesis, etc.**

Enhance Reactants production

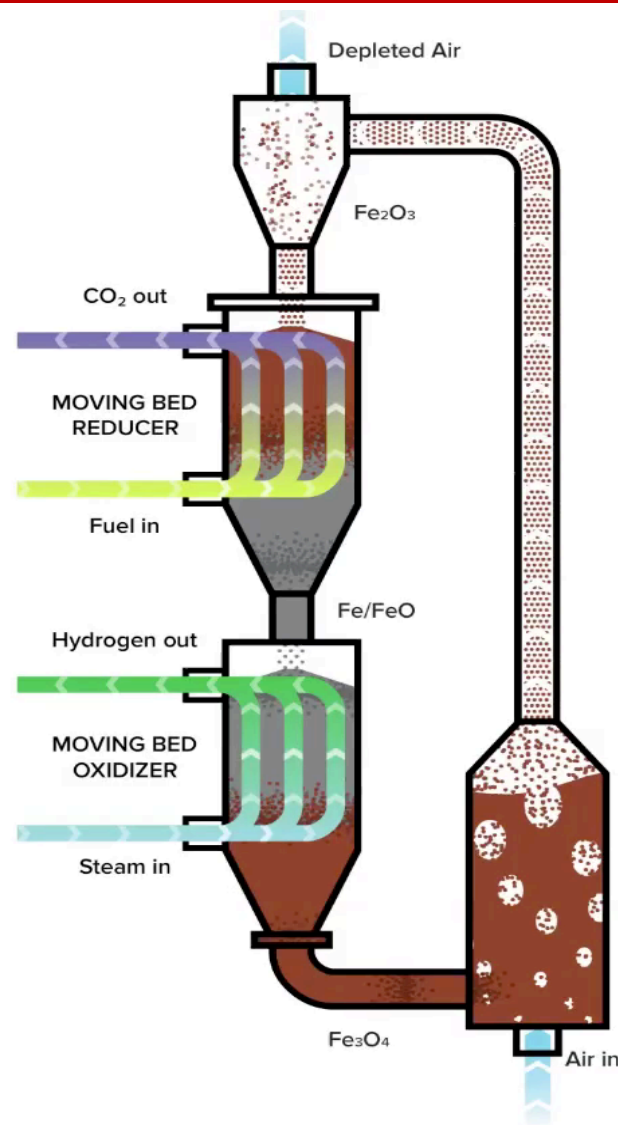
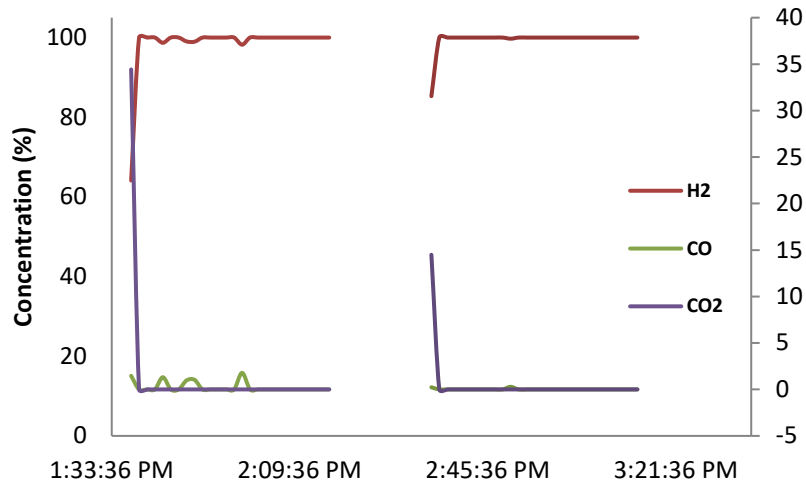
- Use of **renewable electricity for ASU** (N_2 production).
- **Retrofit CO_2 capture systems** for CO_2 capture and sequestration.
- Alternative synthesis route for H_2 production – **Renewable H_2 by electrolysis, biomass to H_2 , Chemical Looping H_2 production, etc.**

Chemical Looping H₂ Production

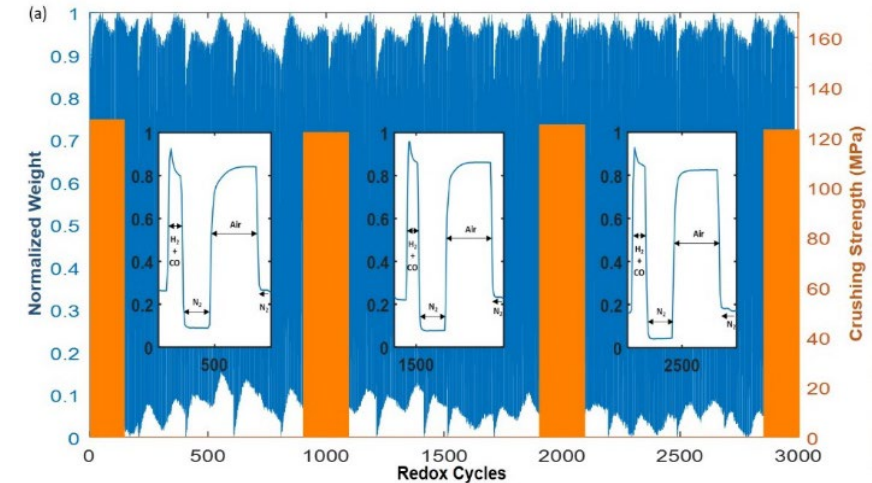
> 99% CO₂ purity in Reducer



>99.99% H₂ purity in Oxidizer



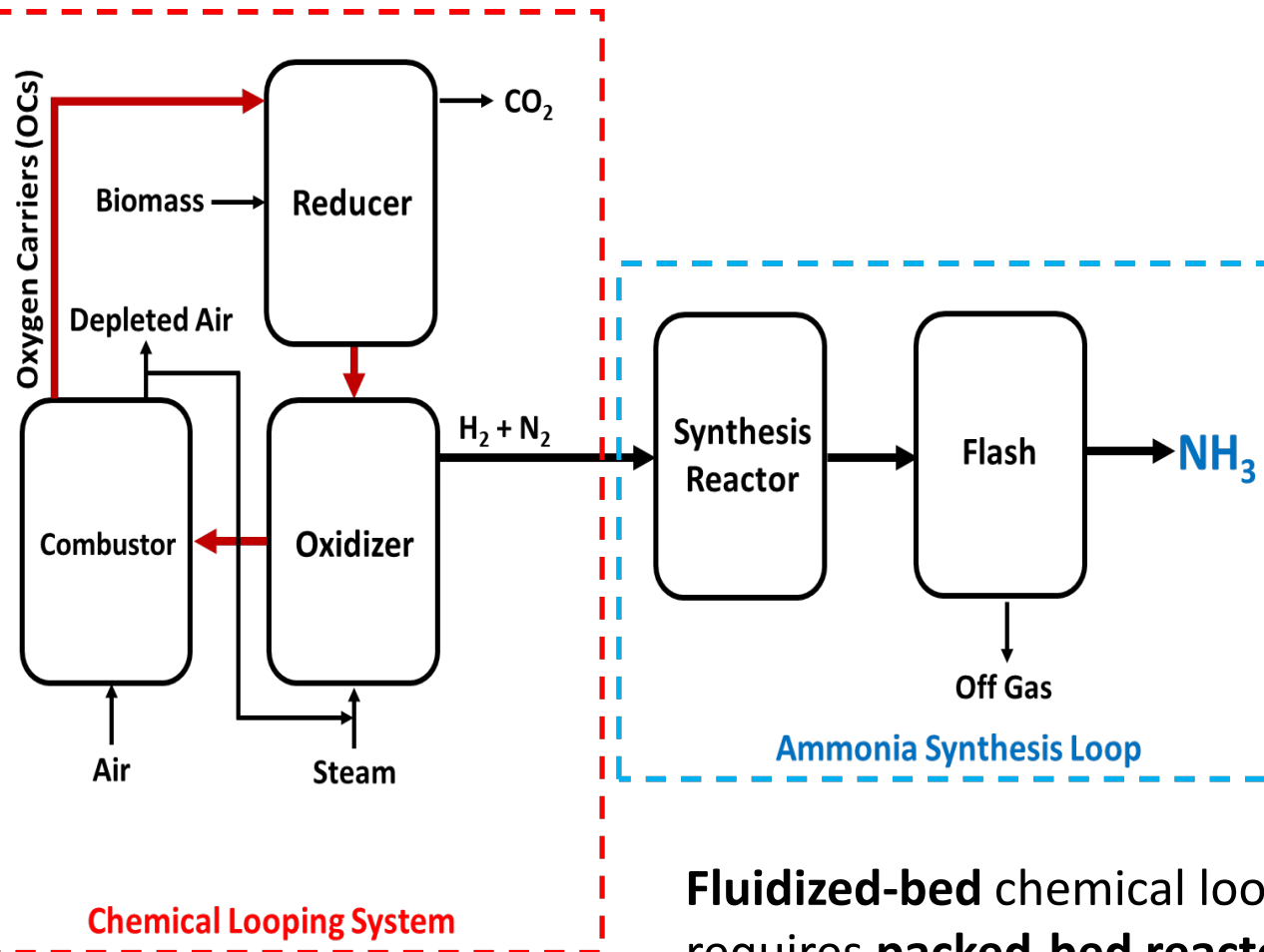
250 kW_{th} Pilot demonstration at the National Carbon Capture Center, AL



Commercial unit being built at Massillon, OH, with 2-10 tons/day H₂ capacity.

Proposed Process

Integrated Biomass Chemical Looping process (CL-3R)



- Involves a 3-reactor chemical looping system and NH_3 synthesis loop, requiring a total of **4 reactors** only.
- Uses **biomass** (carbon-neutral feedstock) as raw material.
- Can be operated for **fuel flexibility**.
- **Autothermal** system, no external heat required for CL process.
- Inherent **sequestration-ready CO_2** stream.

Fluidized-bed chemical looping systems cannot achieve this process scheme; it requires **packed-bed reactors (moving-bed or fixed-bed)**.

Process Development Strategy

3 Step Approach

Process Simulations

- Optimize process conditions
- Generate an optimized process flowsheet

Experimental Evaluation

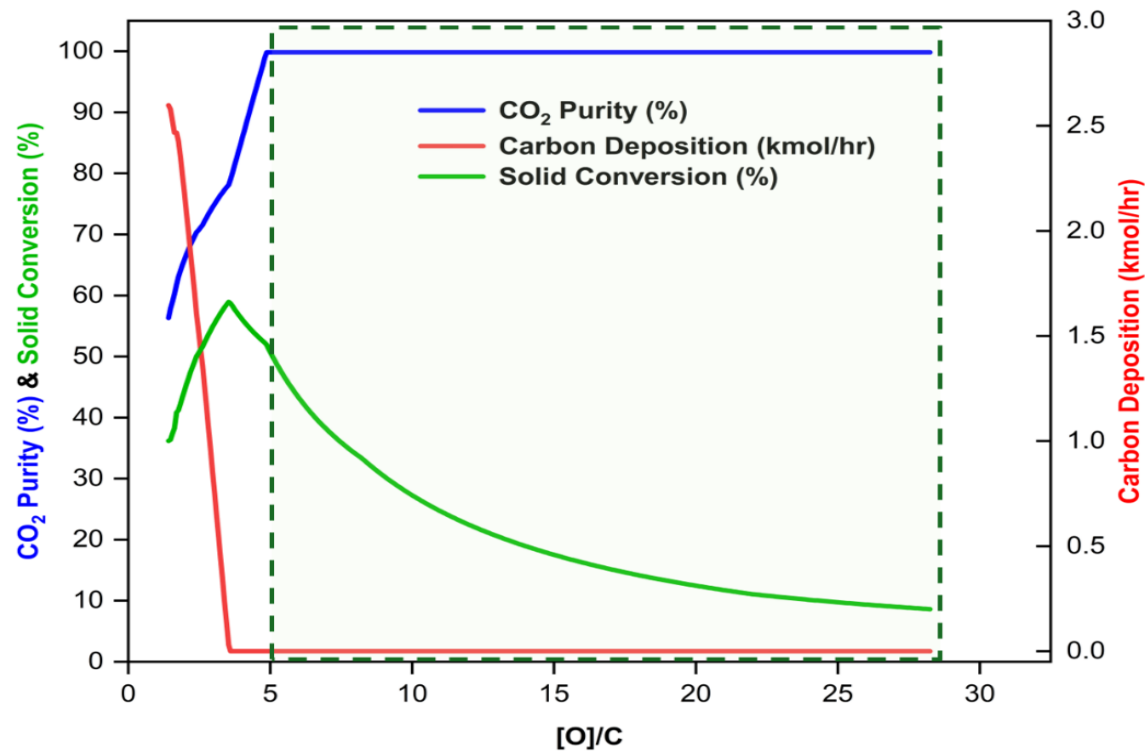
- Experimentally validate simulation predictions

Techno-Economic Analysis

- Calculate CAPEX, OPEX, and MSP
- Analyze the sensitivity of key economic factors

Process Simulation Analysis

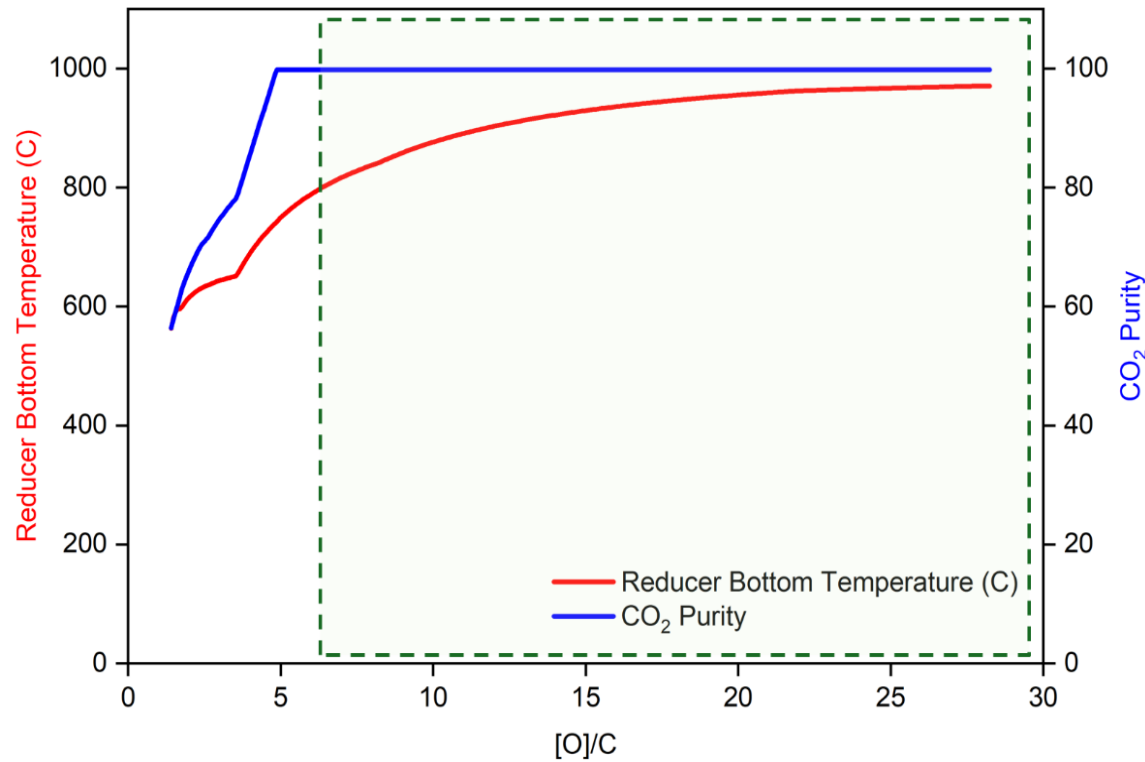
1. CO₂ purity & Carbon Deposition



- Varying [O]/C ratio for the reducer reactor.
- Favorable operating condition:
 - **Carbon Deposition = 0**
 - **CO₂ purity = 100 %**
- Operating Zone: **[O]/C > 5**

Process Simulation Analysis

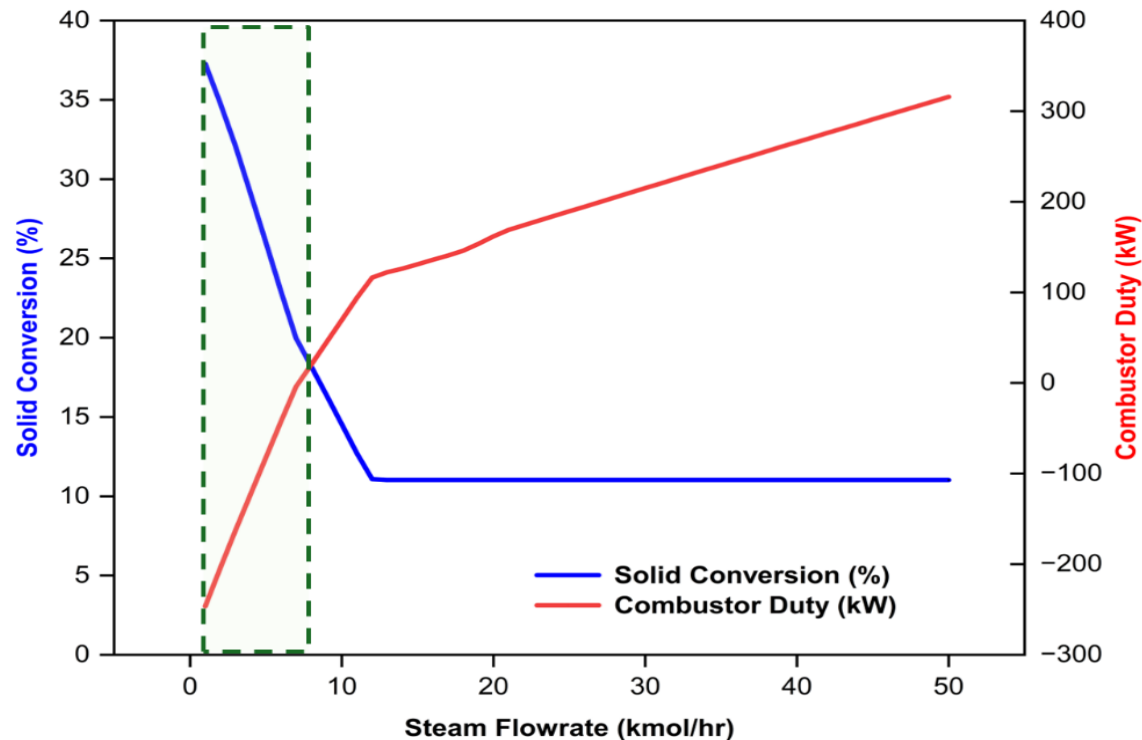
2. Reducer Bottom Temperature



- Varying [O]/C ratio for the reducer reactor.
- Favorable operating condition:
 - **Reducer Bottom Temp. > 800 °C**
- Operating Zone: **[O]/C > 6**
- The lowest OC flow rate that fulfills the above criteria is selected to maximize solids reduction and minimize subsequent reactor volume.

Process Simulation Analysis

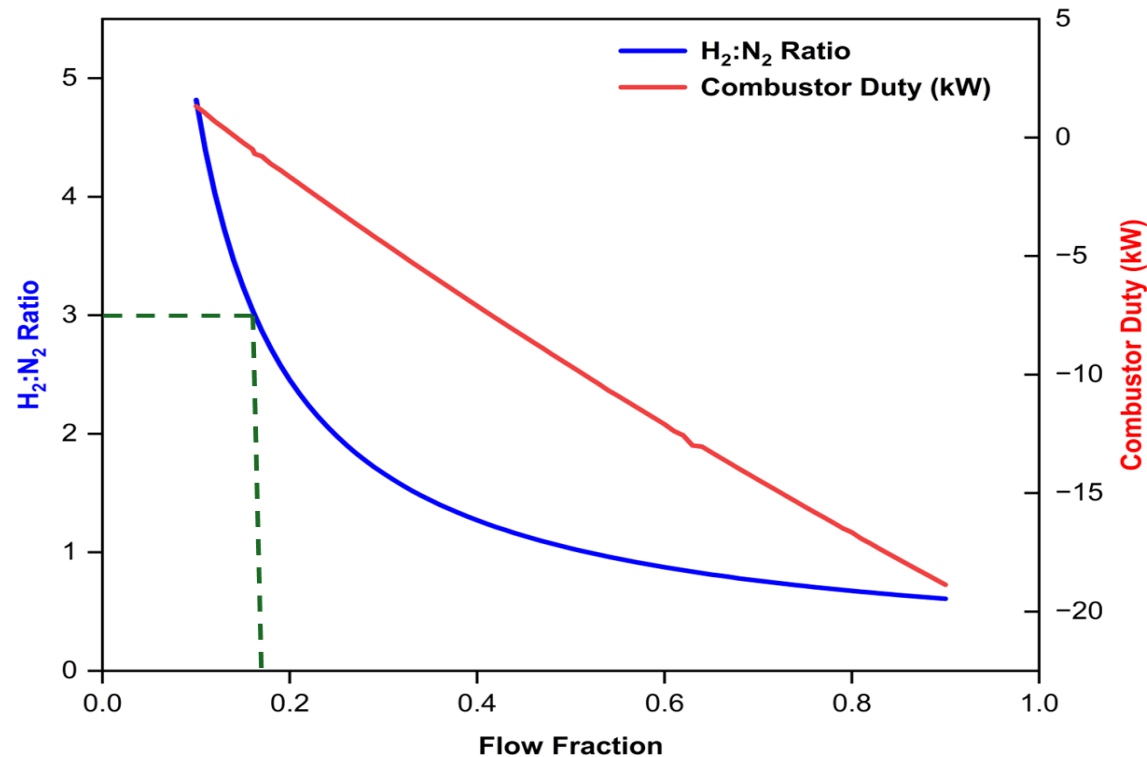
3. Autothermicity



- Varying steam flow rate for oxidizer reactor.
- Favorable operating condition:
 - **Combustor Duty < 0 kW**
- Operating Zone: **Steam flow rate < 8.1 kmol/hr** for 100 kg biomass basis.
- The highest steam flow rate that satisfies the above condition is selected to maximize hydrogen production.

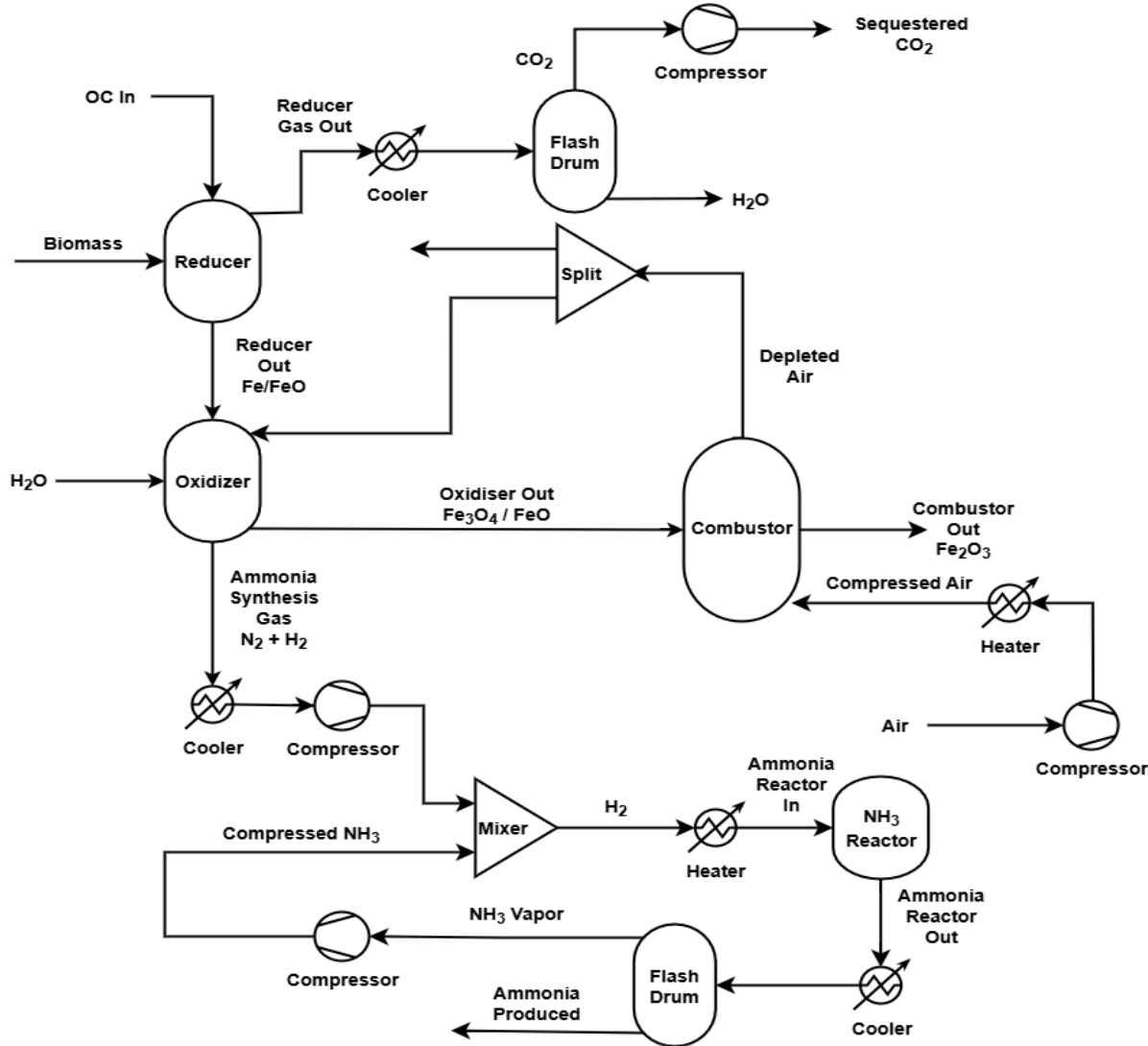
Process Simulation Analysis

4. H_2/N_2 ratio



- Varying depleted air flow fraction.
- Favorable operating condition:
 - $H_2/N_2 = 3$
- Operating Zone: **Flow Fraction = 0.1625**
- The above flow fraction of the depleted air stream is sent to the oxidizer reactor.

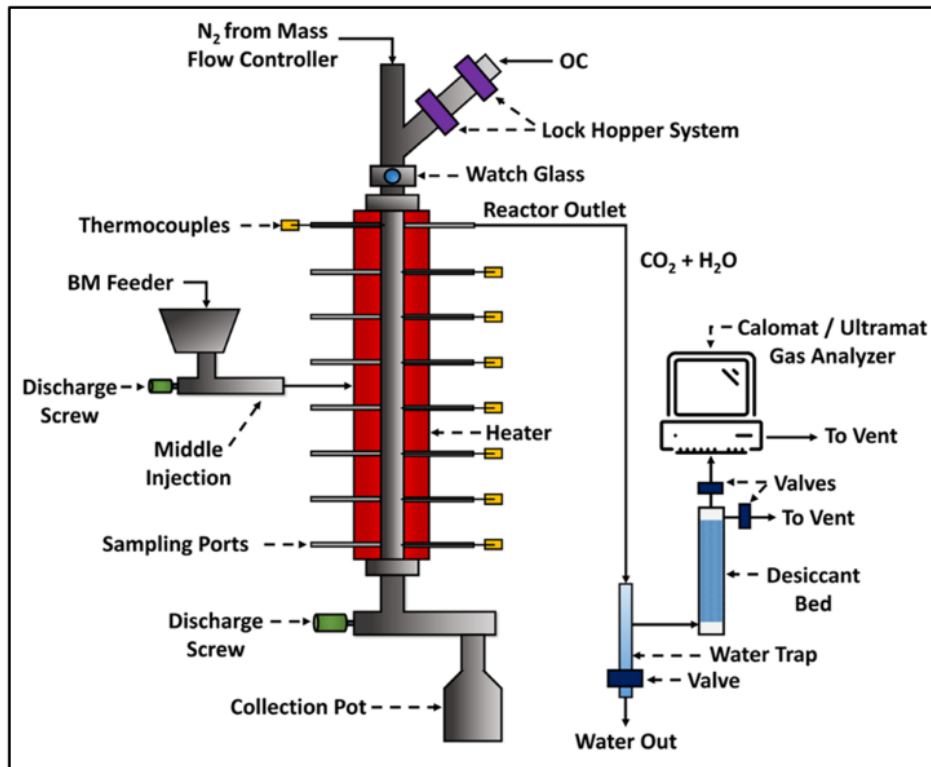
Process Simulation Analysis



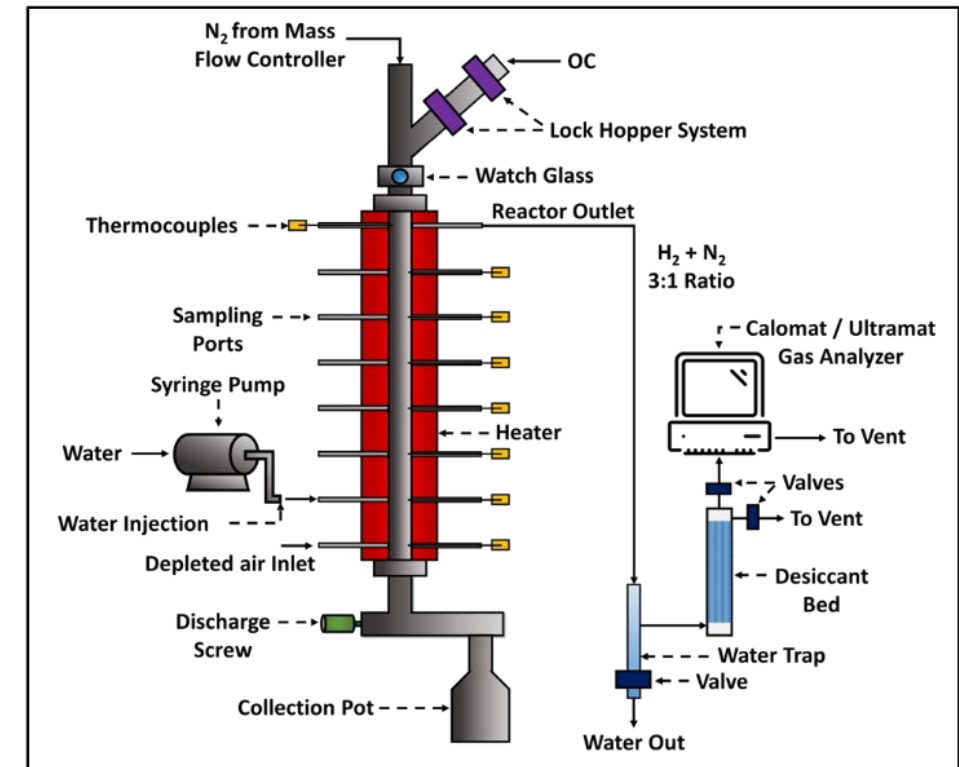
- Optimized flowsheet is **integrated with the Haber-Bosch process** to analyze the ammonia yield.
- Absence of oxidizing species in the NH₃ synthesis gas ensures **no pre-processing** before the Haber-Bosch process.
- The flowsheet is scaled up to **3900 tons/day NH₃** production and used for further Techno-Economic Analysis.
- A scaled-down version of the flowsheet is used to extract process conditions such as flow rates, temperatures, etc., for Experimental Analysis.

Experimental Analysis

Experimental Setup



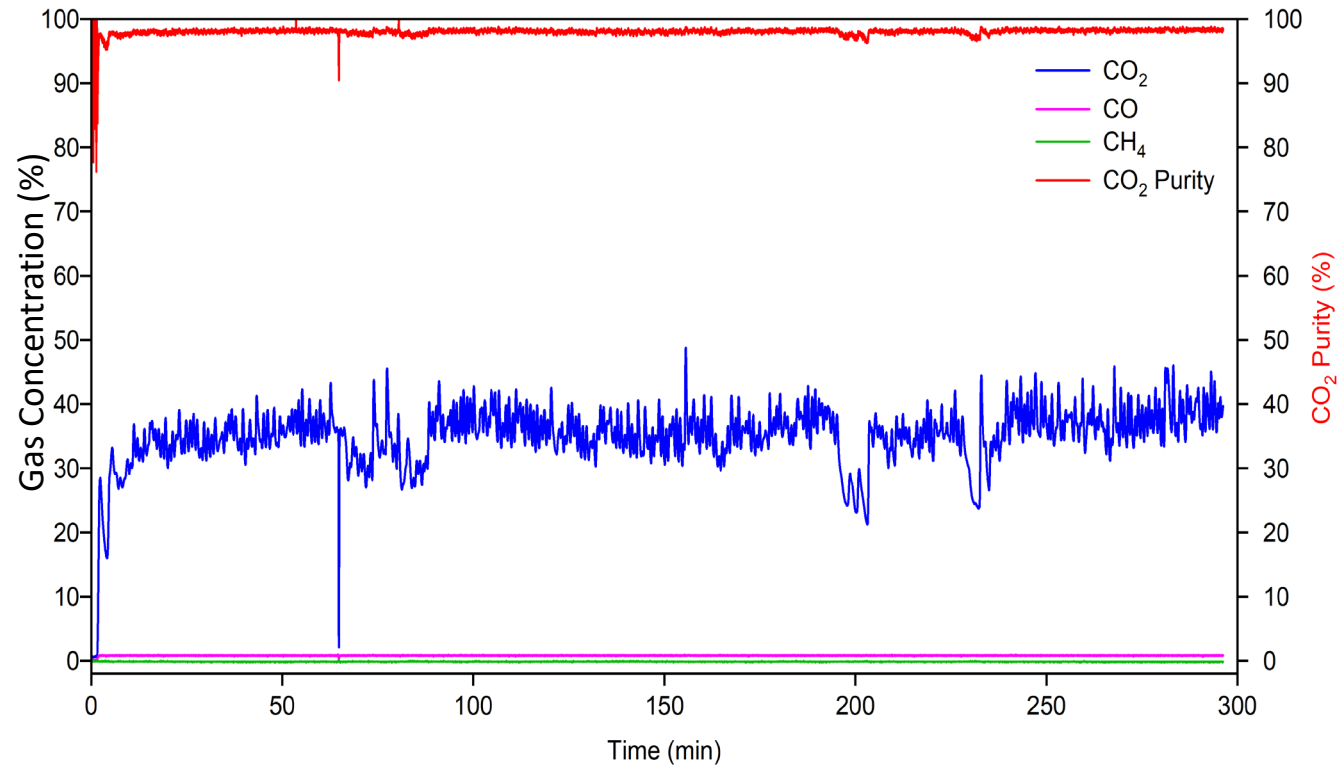
Reducer Reactor



Oxidizer Reactor

Experimental Analysis

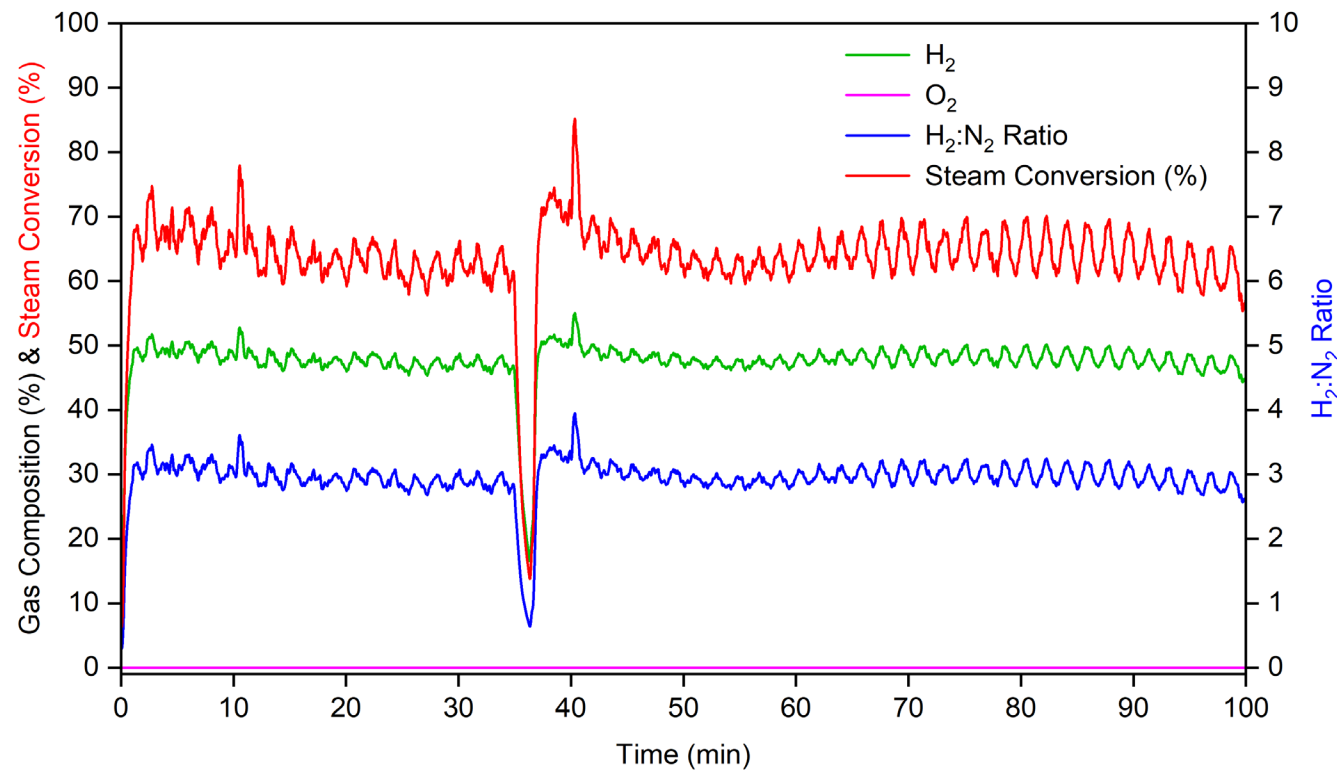
Reducer Reactor



- **≈100 % CO₂ purity.**
- Stable gas concentration profile for nearly 300 minutes (4 times Solids Residence Time).
- **100 % biomass conversion**, aligning with thermodynamic simulations.
- **≈45 % solids reduction.**

Experimental Analysis

Oxidizer Reactor



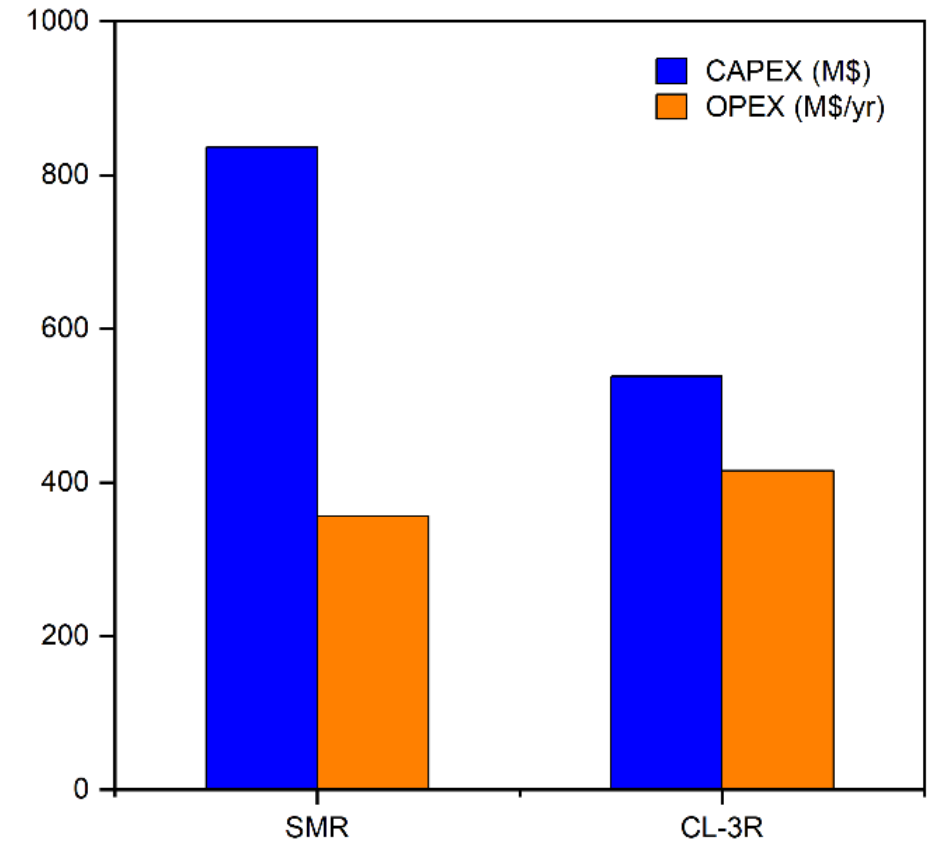
- Stable gas concentration profile for 100 minutes (2 times Solids Residence Time).
- **H₂/N₂ ratio of ≈ 3** , essential for NH₃ synthesis.
- **≈ 65 % steam conversion**, aligning with thermodynamic simulations.
- **≈ 20 % solids reduction** at outlet.
- **0% oxygen** throughout, protecting Haber-Bosch catalyst.

Techno-Economic Analysis

Key TEA considerations

- Base year = 2018
- Plant Capacity = 3900 tons/day NH_3
- Cost of feedstock:
 - Natural Gas = \$4.42/MMBTU
 - Corncob = \$63/ton
- OC attrition rate = 0.0114%
- Internal Rate of Return = 10%
- Value of tax credits:
 - 45Q = \$85/ton of CO_2
 - 45V = \$3/kg of H_2
- Tax Rate = 35%
- Cost estimates for equipment were obtained from NETL baseline reports, which were further scaled based on corresponding parameters and scaling exponents.

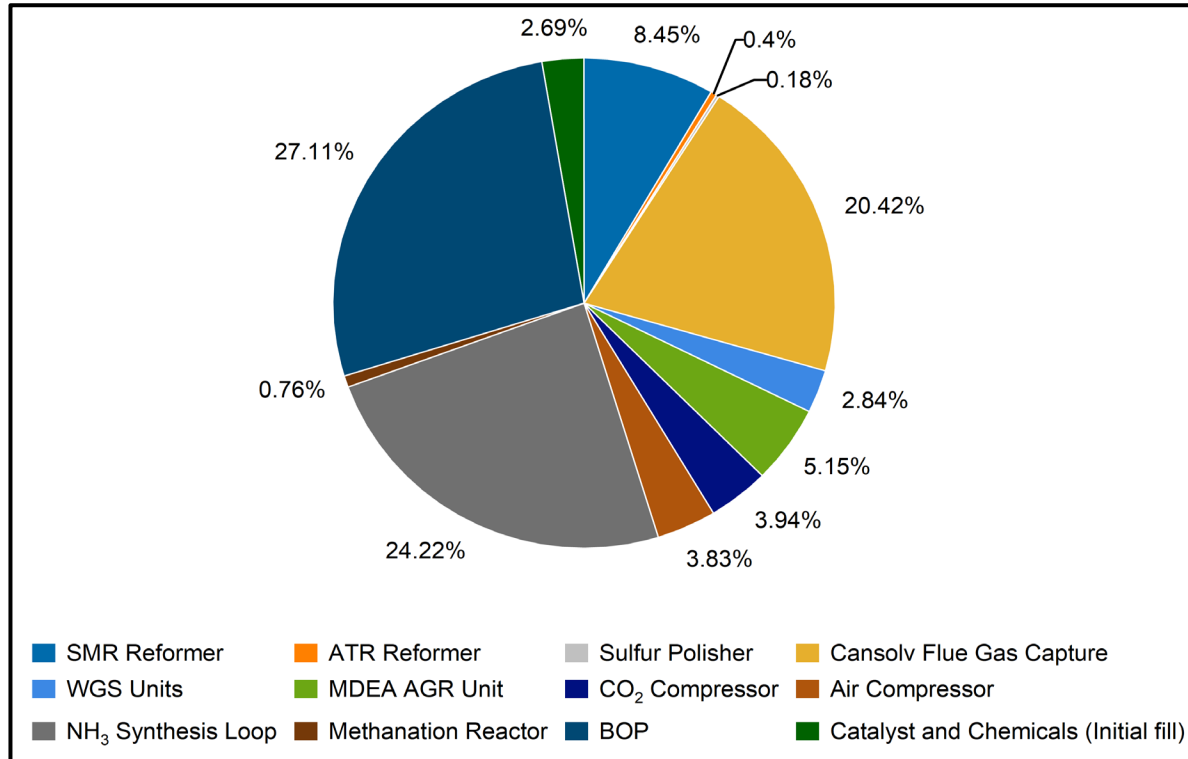
Comparison for CAPEX & OPEX



CL3R shows **36% lower CAPEX**, but **16% higher OPEX** than SMR.

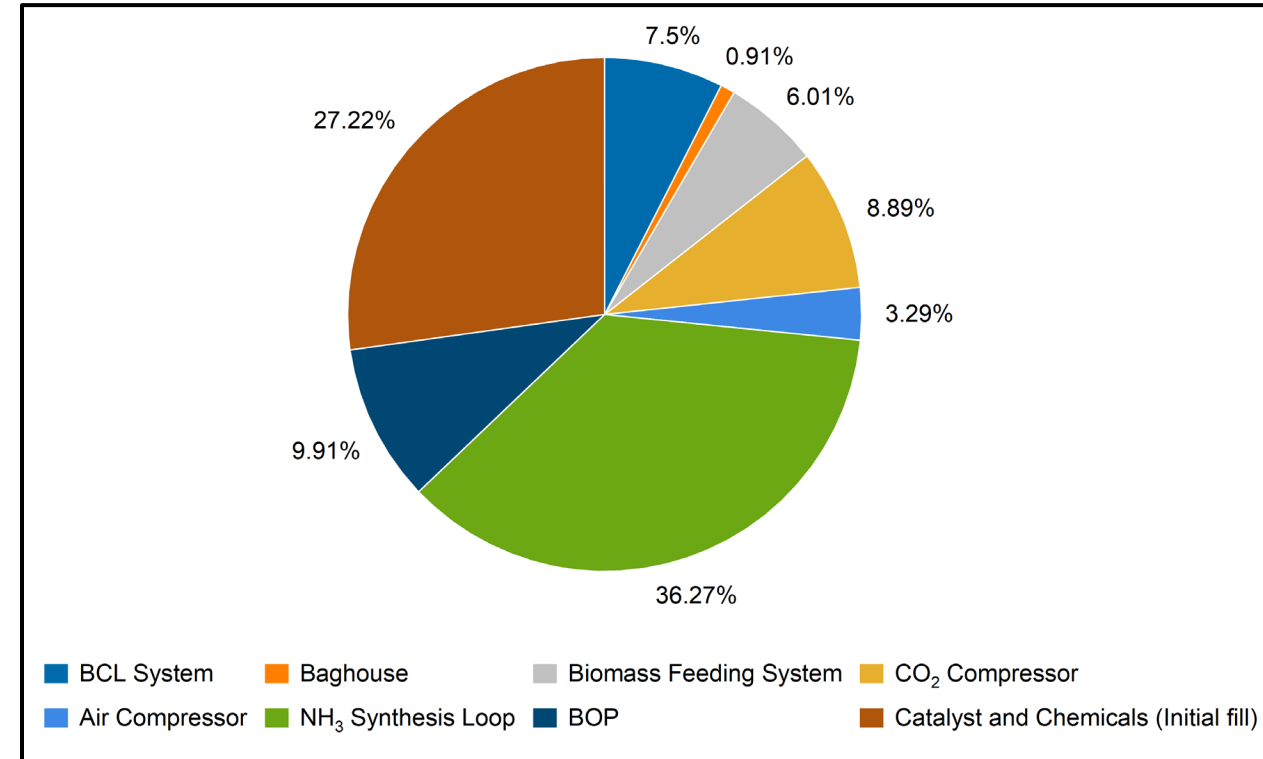
Techno-Economic Analysis

Distribution of CAPEX



SMR

1. NH₃ synthesis Loop (24.2%)
2. Cansolv Flue Gas Capture (20.4%)
3. SMR reformer (8.45%)

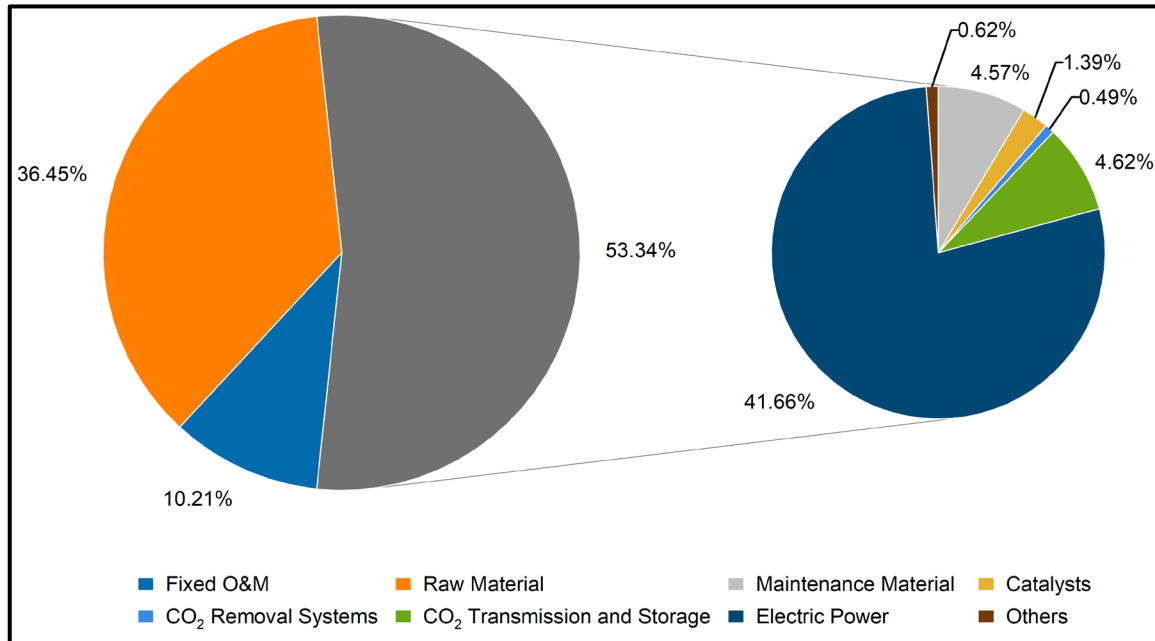


CL-3R

1. NH₃ synthesis Loop (36.3%)
2. Initial catalyst fill [mainly OCs] (27.2%)
3. CO₂ compressor (8.89%)

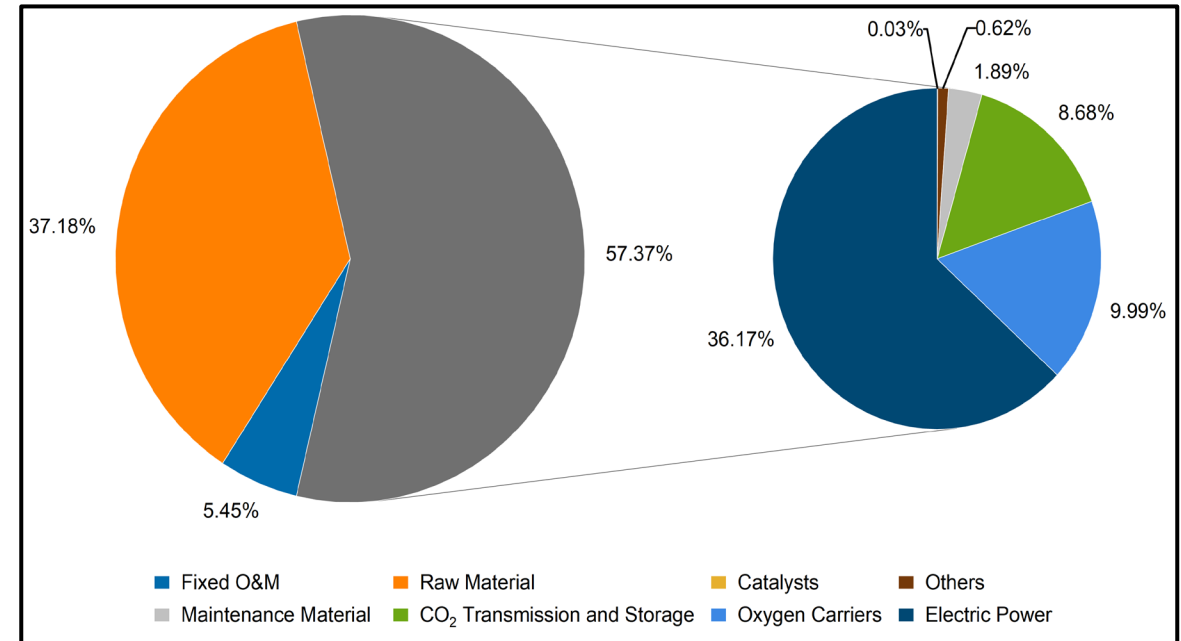
Techno-Economic Analysis

Distribution of OPEX



SMR

1. Electric Power (41.7%)
2. Feedstock (Natural Gas) (36.5%)
3. Fixed O&M (10.21%)



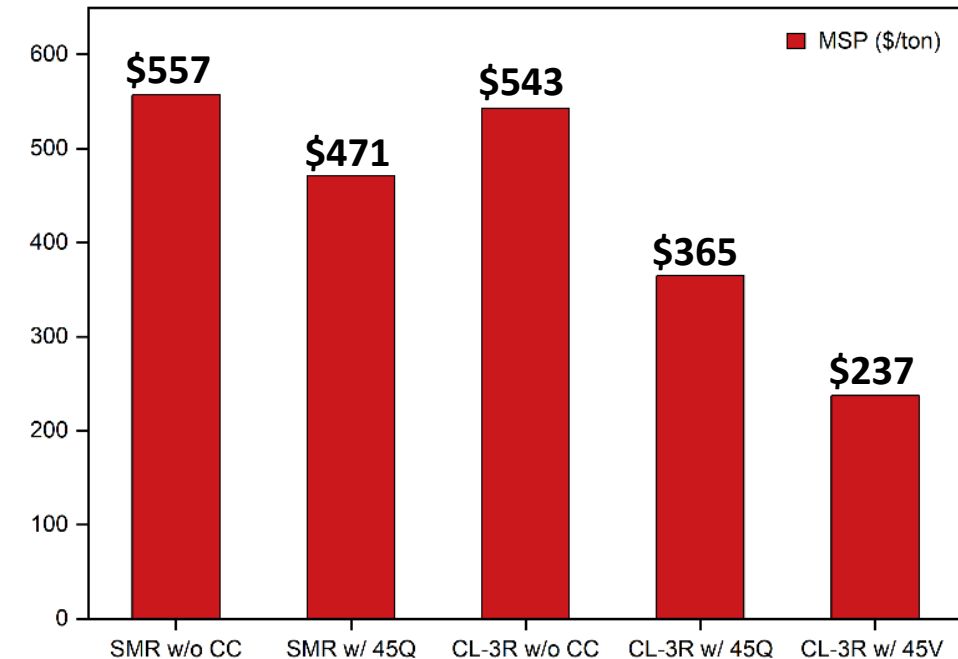
CL-3R

1. Feedstock (Corncob biomass) (37.2%)
2. Electric Power (36.2%)
3. OC refill (9.99%)

Techno-Economic Analysis

Minimum Selling Price (MSP)

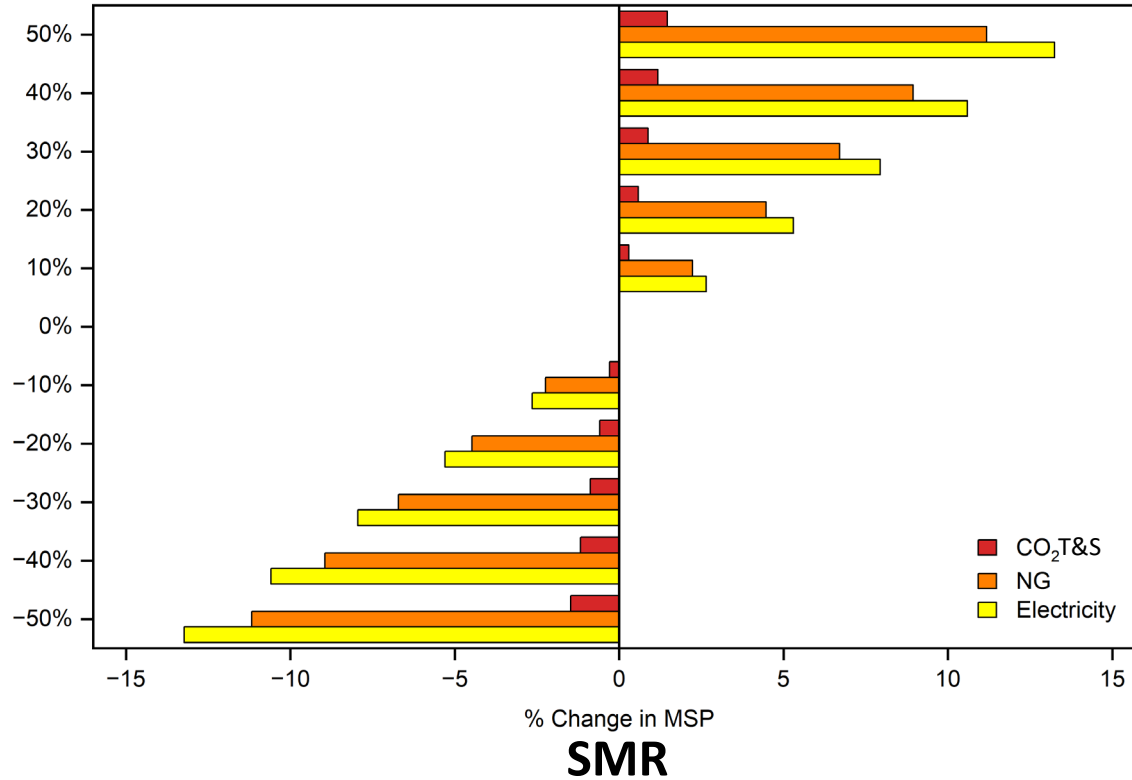
1. *Annual income = Income from NH_3 sales + 45 V/45 Q credits*
2. *Annual production costs*
= Raw Material costs + Fixed O&M Costs + Variable O&M Costs
3. *Annual Cash Income*
= Annual income – (Annual production costs + Loan payment + Income Tax)
4. *Annual Present Value = Annual Cash Income * Discount factor*
5. *Net Present Value for n^{th} year = $\sum_1^n \text{Annual present value}$*
6. *Net Present Worth*
= Net Present Value for plant lifetime – (Total Capital Investment + Interest)
7. *MSP is determined iteratively by changing the selling price of ammonia until the NPW of the plant is zero.*



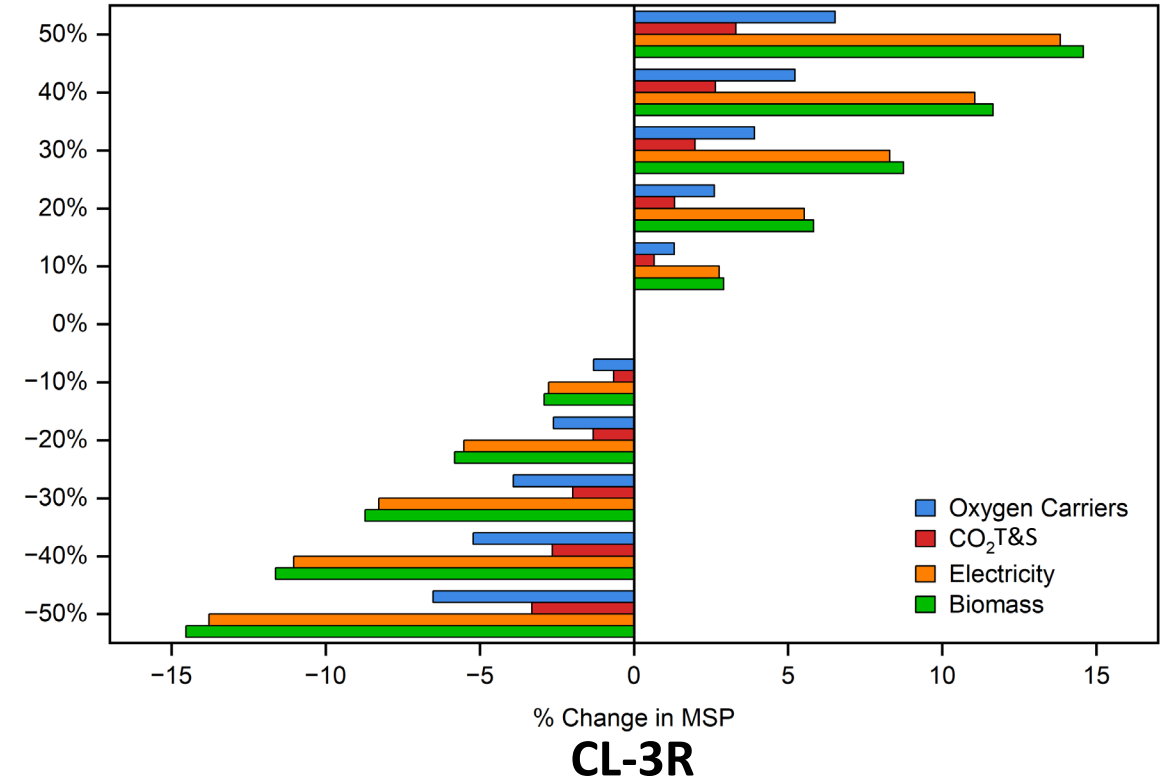
A 50.3% lower MSP can be obtained using the CL-3R process as compared to the SMR process.

Techno-Economic Analysis

Sensitivity Analysis w.r.t OPEX factors



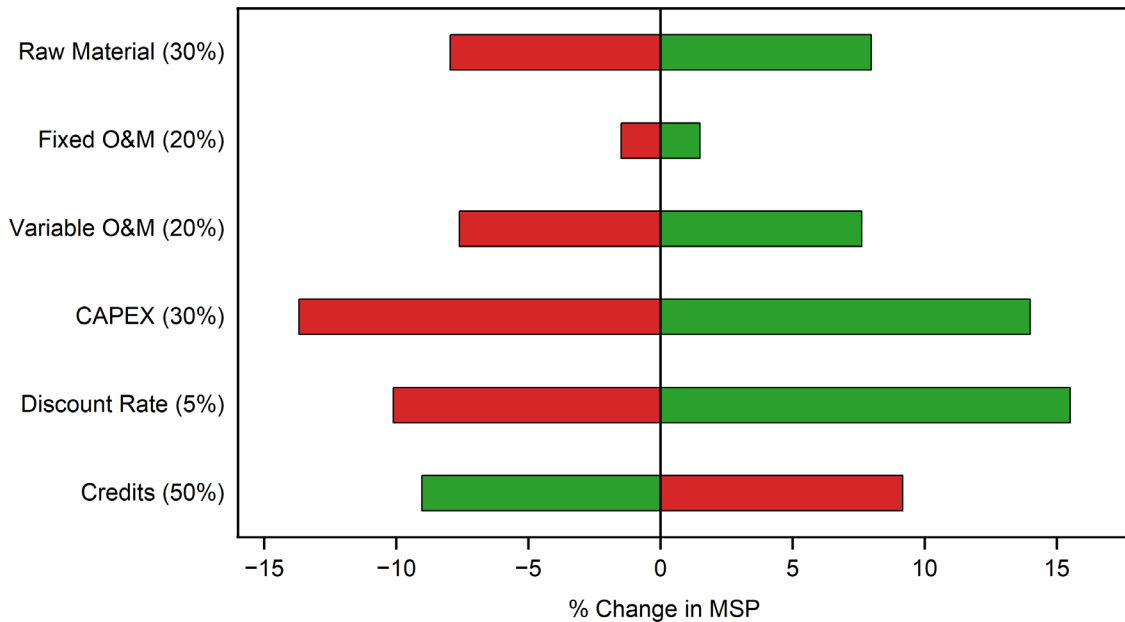
Sensitivity:
Electricity > Natural Gas > CO₂ T&S



Sensitivity :
Biomass > Electricity > OC > CO₂ T&S

Techno-Economic Analysis

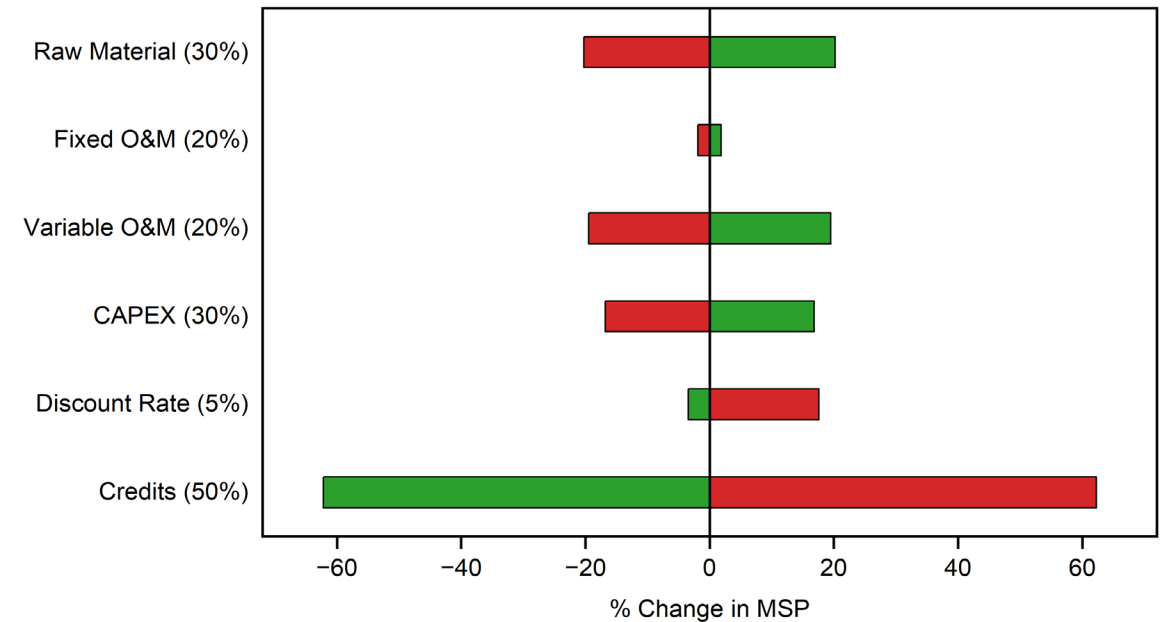
Sensitivity Analysis w.r.t key economic parameters



SMR

Sensitivity:

CAPEX > Discount Rate > Raw Material



CL-3R

Sensitivity :

Credits > Variable O&M > Raw Materials

Conclusions

- The Integrated Biomass Chemical Looping process generates a pure stream of H_2/N_2 in a 3:1 molar ratio, while simultaneously producing a sequestration-ready CO_2 stream, providing an excellent alternative to SMR-based ammonia production process.
- The CL3R process is successfully optimized on ASPEN Plus software, and subsequently experimentally validated, with results showing 100 % CO_2 purity in the reducer reactor and a 3:1 $\text{H}_2:\text{N}_2$ ratio in the oxidizer reactor.
- The techno-economic analysis reveals that ammonia production using the CL3R process can reduce the minimum selling price by up to 57.5%.

Future Work



- Scale-up the technology to TRL 4-5 using continuous sub-pilot operation.
- Test for micro-emissions from the reducer reactor for solid fuels.
- Test for fuel flexibility with continuous operation.

Acknowledgements



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Linked in



THANK YOU!!