

MEMBRANE
PSA
HYDROGEN
STEAM REFORMING
CRYOGENIC GAS PURIFICATION
HYDROPRIME® MAX
LINDE AMMONIA CONCEPT
POLY-GENERATION PLANTS
SYNGAS AND CARBON MONOXIDE
CCS/U

DRYREF™ & SYNSPIRE™

Innovation for HyCO applications

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Global Syngas Conference, 2020

Making our world more productive



Agenda.



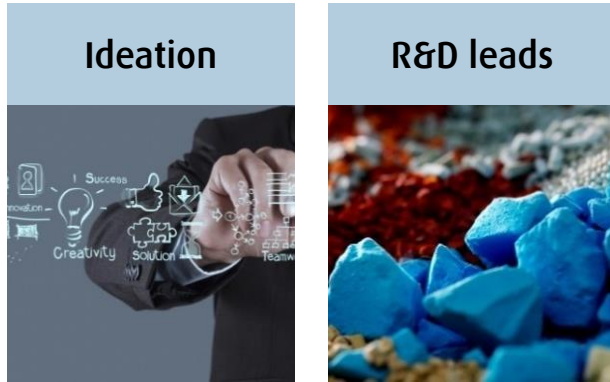
1. BASF & LINDE: Innovation through partnership
2. Process Introduction
3. Case Evaluation
4. CO₂ Footprint
5. Applications
6. Summary

Agenda.

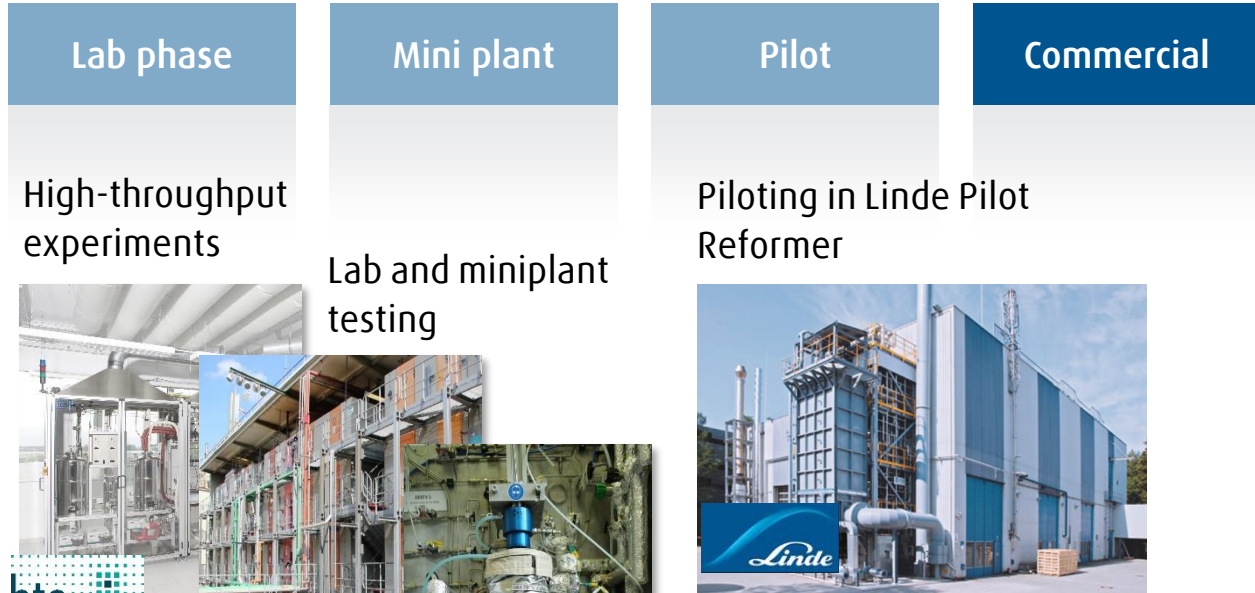


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Joining forces for the development of a unique catalyst for dry reforming: a long-term journey



Joint Development



Partnering with aknowledged R&D institute and universities



First commercial reference in industrial Linde HyCO unit 08/2017-07/2018 Full product utilization

Funded by BMBF under: 03ET1282 & 0327856

Agenda.



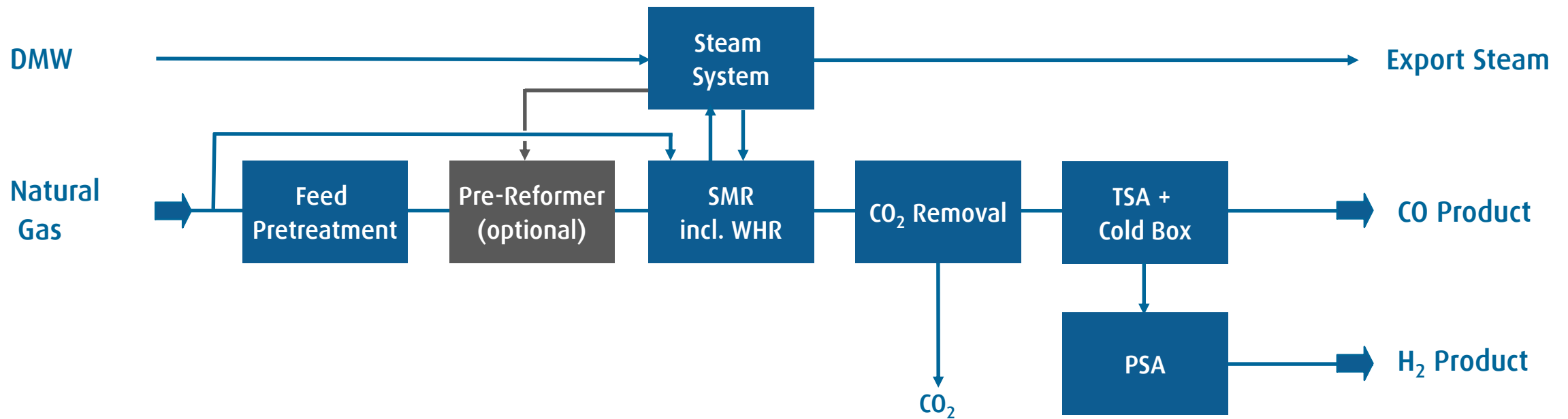
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Process Introduction

Simplified process arrangement



- Simplified typical process arrangement based on natural gas as feedstock and Steam Methane Reforming (SMR)
- Pre-reformer as optional equipment
- H₂/CO product ratio as target



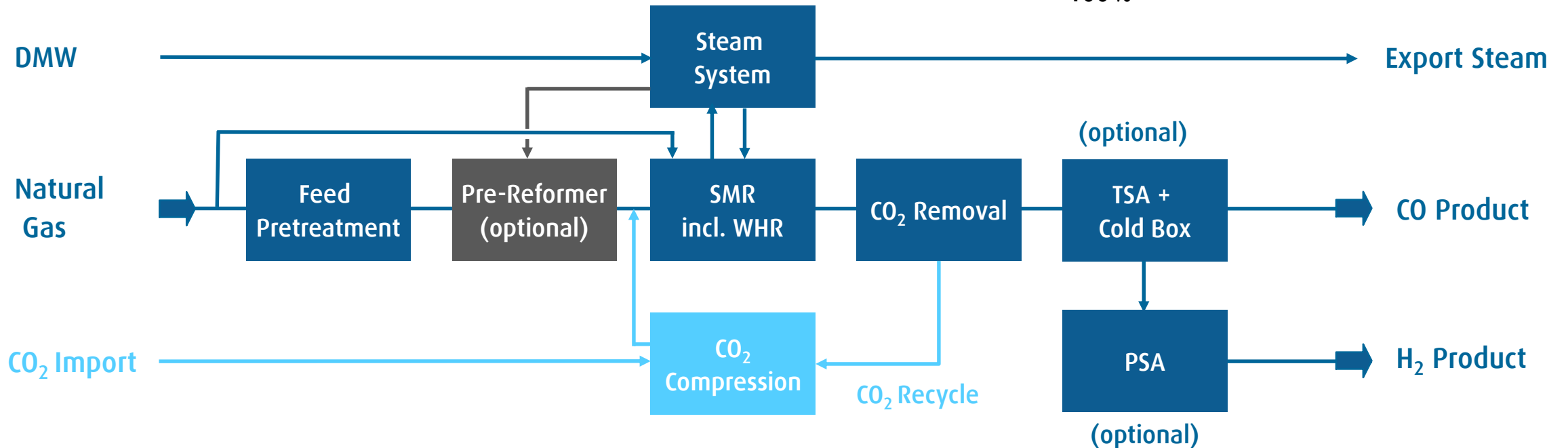
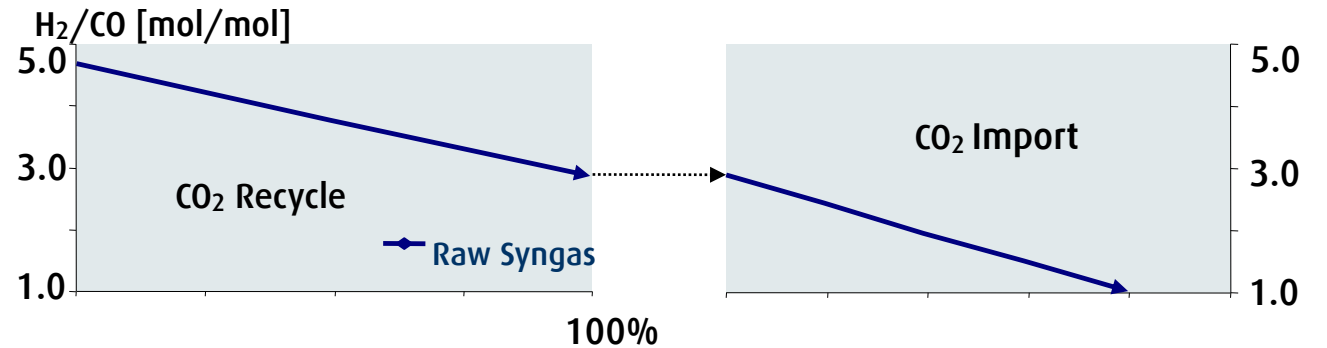
Process Introduction

CO₂ recycle and CO₂ import



How to adjust H₂/CO ratio in syngas?

- CO₂ recycle for reduction of H₂/CO ratio
- CO₂ import for full flexibility of H₂/CO product ratio



Process Introduction

DRYREF™ process arrangement

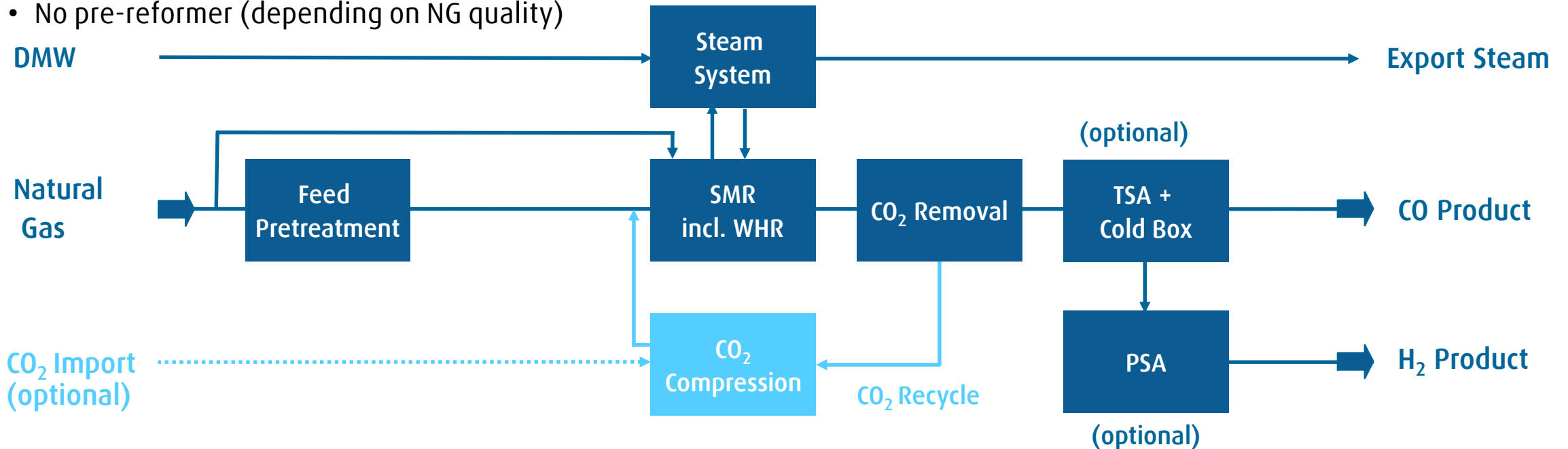


- Application:

- DRYREF process is typically used for natural gas based H₂+CO plants
- CO₂ recycle to SMR with optional additional CO₂ import

- Key advantages:

- DRYREF catalyst allows lower S/C ratio which improves OPEX and energy efficiency
- No pre-reformer (depending on NG quality)



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Case Evaluation

Scenario 1 – without CO₂ import



Conventional process

- Steam to process: S/C 2.5 mol/mol
- Full CO₂ recycle
- No additional equipment

Conventional process incl. Pre-Reformer

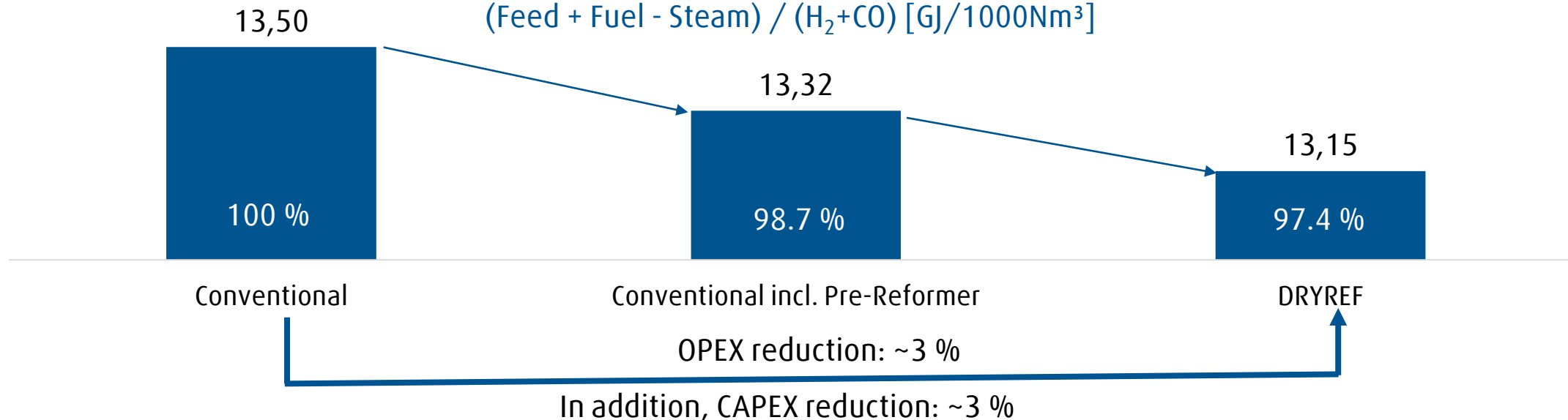
- Steam to process: S/C 2.0 mol/mol
- Full CO₂ recycle
- Additional equipment: Pre-Reformer

DRYREF process

- Steam to process: S/C 1.5 mol/mol
- Full CO₂ recycle
- BASF catalyst (SYNSPIRE™ G1-110)
- No additional equipment

Conditions are resulting in H₂/CO product ratio of 2.45 mol/mol

Specific energy consumption as
(Feed + Fuel - Steam) / (H₂+CO) [GJ/1000Nm³]



Case Evaluation

Scenario 2 – including CO₂ import



Conventional process

- Steam to process: S/C 2.5 mol/mol
- Full CO₂ recycle + CO₂ import
- No additional equipment

Conventional process incl. Pre-Reformer

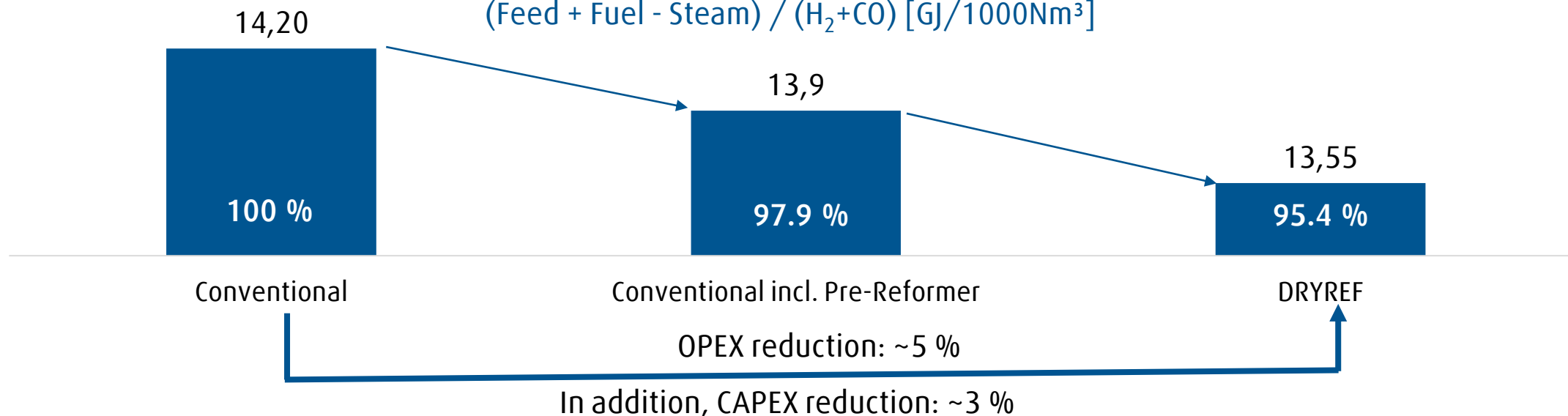
- Steam to process: S/C 2.0 mol/mol
- Full CO₂ recycle + CO₂ import
- Additional equipment: Pre-Reformer

DRYREF process

- Steam to process: S/C 1.5 mol/mol
- Full CO₂ recycle + CO₂ import
- BASF catalyst (SYNSPIRE™ G1-110)
- No additional equipment

H₂/CO product ratio of 1.5 mol/mol adjusted by CO₂ Import

Specific energy consumption as
(Feed + Fuel - Steam) / (H₂+CO) [GJ/1000Nm³]



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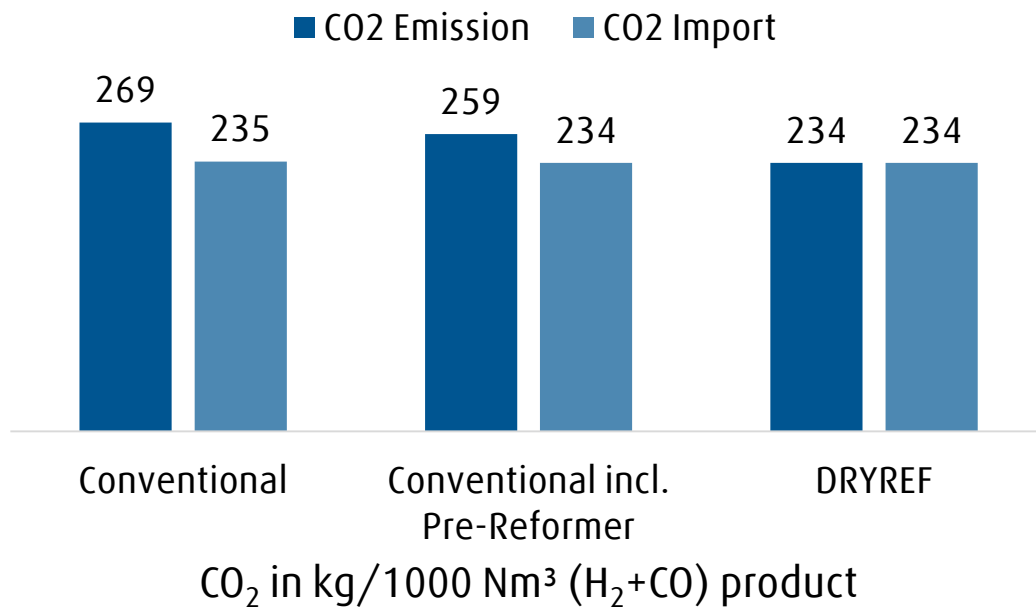
CO₂ Footprint

DRYREF as CO₂ consuming process

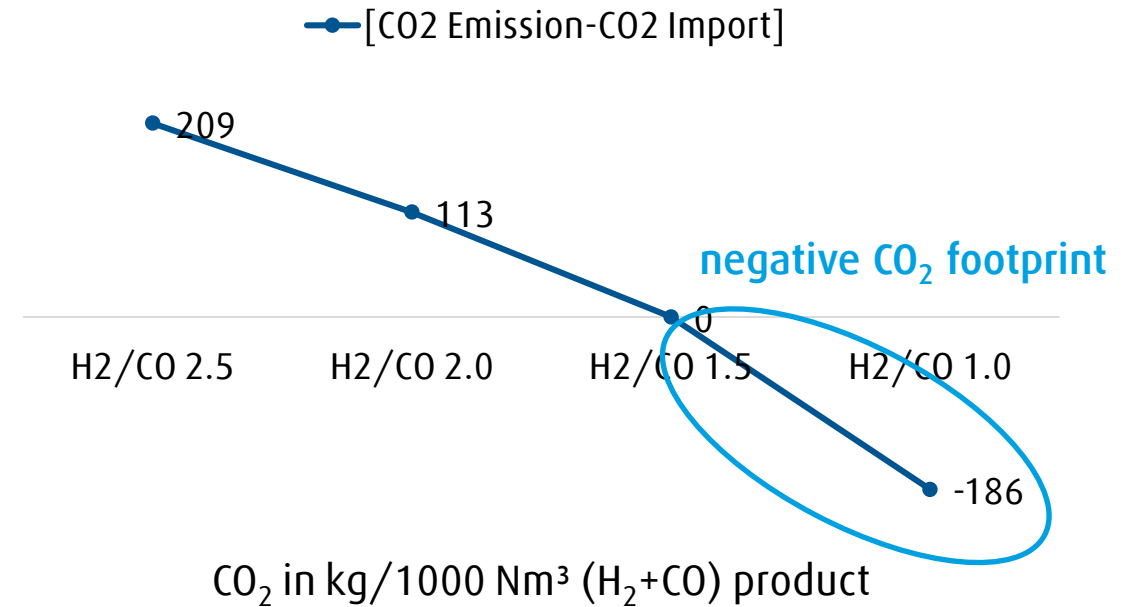


- CO₂ Import is used to compensate direct CO₂ emissions from reformer flue gas
- Plant design for high air preheat temperature and minimum steam production
- Break-even to negative CO₂ emissions for DRYREF at H₂/CO product ratio of 1.5 (molar basis)

CO₂ footprint comparison at H₂/CO=1.5



CO₂ footprint for DRYREF process



Agenda.



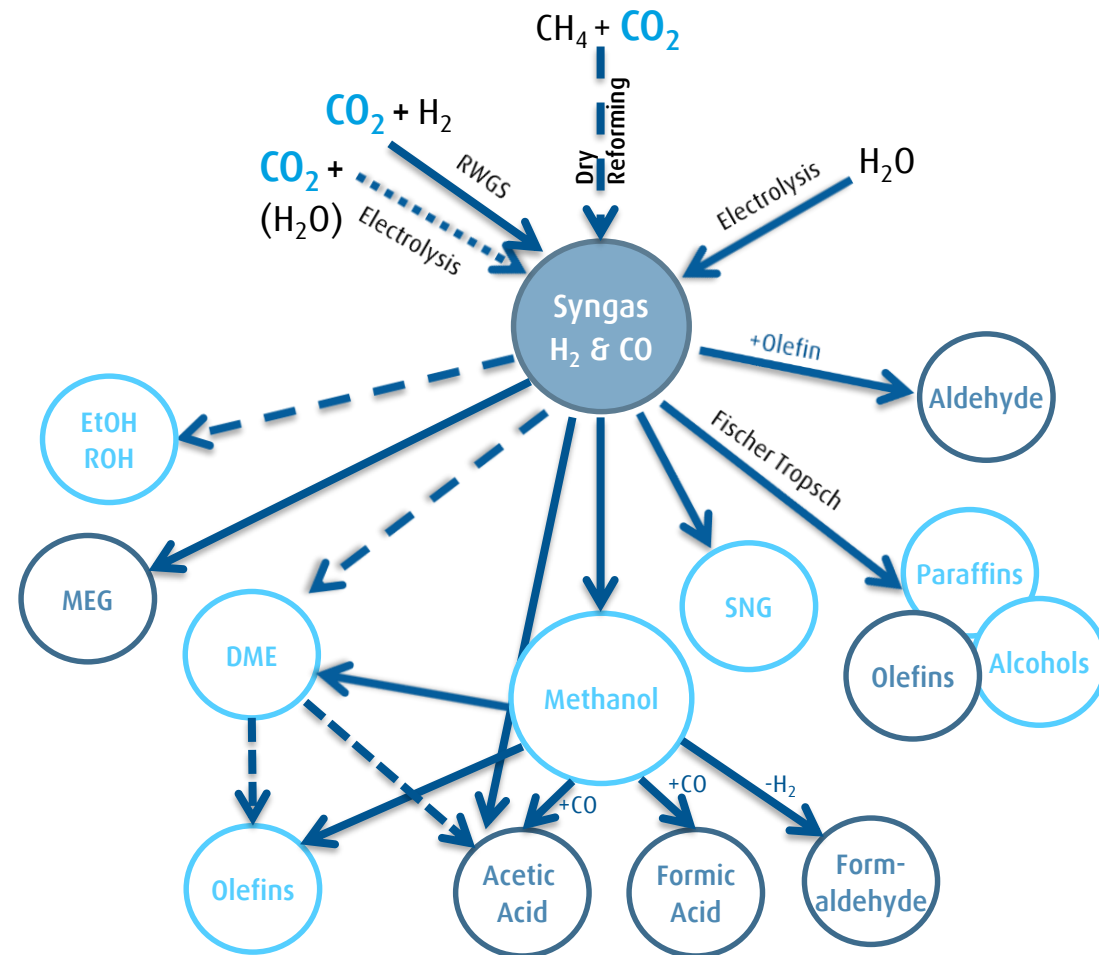
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Applications

DRYREF advantages can be obtained in many applications



- Most syngas downstream processes require SN=2 or below
- Hence, efficiency gain by DryRef can be obtained for almost all downstream process integrations compared to conventional SMR
- Applications such as acetic acid, formic acid production, MEG and hydroformylation to aldehydes have overall H₂/CO demand of 1
- Hence, these downstream needs can be addressed with negative CO₂ footprint – already now!



H₂/CO < 2

H₂/CO ≥ 2

Commercial / Demo

Lab / Pilot

Basic Research

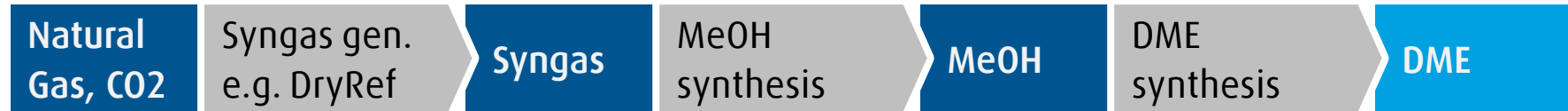
Applications

DRYREF in combination with Direct DME Synthesis



Reference process

Conventional two step route to DME

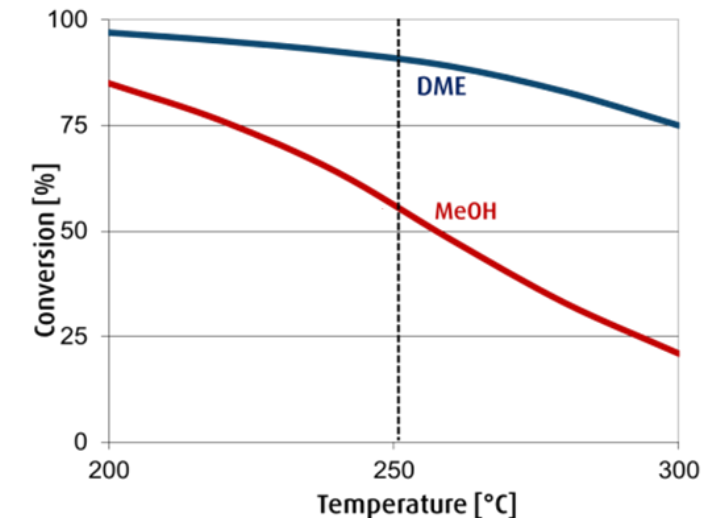


→ Conventional DME production requires **two steps** from syngas including **MeOH synthesis** limited by thermodynamics

Linde-BASF Direct DME



- Linde-BASF Direct DME technology **eliminates one process step** and takes advantage of **favourable thermodynamics** for DME synthesis
- **Specific catalyst developed on-purpose**
- **Many process configurations possible**, CO₂ rich recycle from DME synthesis favors DryRef with Direct DME as best process option for small and medium scale plants



optional

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Summary

- DRYREF process is typically used for natural gas based H₂+CO plants
- BASF catalyst (SYNSPIRE™ G1-110) offers possibility for operation at low S/C ratio without pre-reforming
- Energy Efficiency and OPEX is highly beneficial compared to conventional process arrangements
- CAPEX is highly competitive for new built plants
- CO₂ footprint is beneficial compared to conventional process
- CO₂ footprint is getting negative at H₂/CO product ratios below 1.5 mol/mol and minimum steam production

Outlook

- Each project is different. Linde will provide optimized tailor-made solution for your individual scenario.
- Further fields of DRYREF application:
 - Revamp projects or direct refill (customized scenarios)
 - Efficient production of H₂ with low S/C ratio
 - Even lower OPEX and/or CO₂ emissions for next generation catalyst DRYREF™ SYNSPIRE G2-120 in case of low H₂/CO ratio

Joining forces for the development of a unique catalyst for dry reforming: where are we on our journey?



**SYNSPIRE
G1-110**

Lab phase

High-throughput
experiments

Mini plant

Lab and miniplant
testing

Pilot

Piloting in Linde Pilot
Reformer

Commercial

First commercial reference
Linde HyCO unit
08/2017-07/2018,
full product utilization

open for commercial 3rd
party projects



Piloting in Linde Pilot
Reformer successfully
finished 10/2020

**SYNSPIRE
G2-120**

Lab phase

Mini plant

Pilot

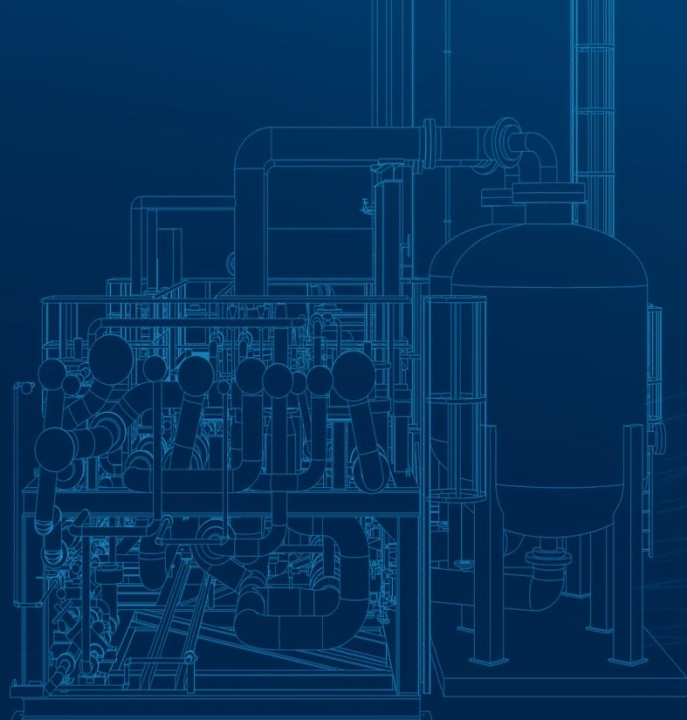
Commercial

Demonstration: open for
partnering

contact Linde Engineering: (1) DRYREF feasibility of your project, (2) demonstration of G2-120, or (3) LPR test campaigns!



DryRef Cobalt catalyst for LPR
DRYREF™ SYNSPIRE G2-120



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Thank you for your attention.

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Making our world more productive

