Air Liquide ENGINEERING & CONSTRUCTION

Cryogenics & Lurgi technologies

A New Reactor Concept for Conversion of CO_2 to Methanol

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ENGINEERING
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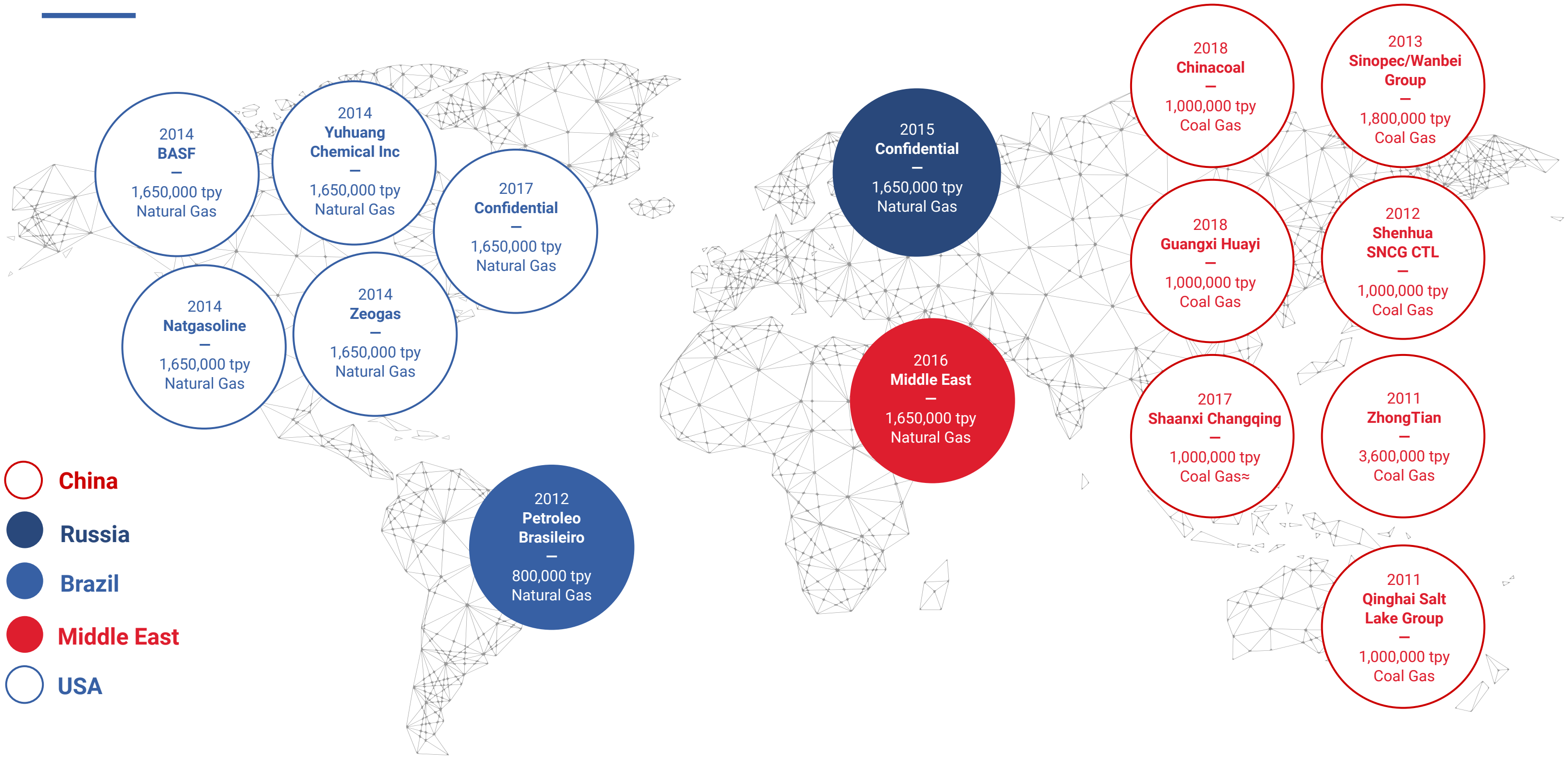
Content

Conventional Methanol Technology

Methanol: **Air Liquide's Track Record**

- **Different feedstocks**
  - Natural gas, naphtha, coal, residue
  - Over 60 licenses: total capacity of 49.0 MMTPY
- **Long-standing cooperation with** CLARIANT
- **Full service portfolio**
  - Licensing + proprietary design
  - Basic + detailed engineering design
  - Construction + commissioning services
  - Provision of industrial gases (O_2, N_2, CO_2, N_2)
- **Extensive R&D facilities at AL**

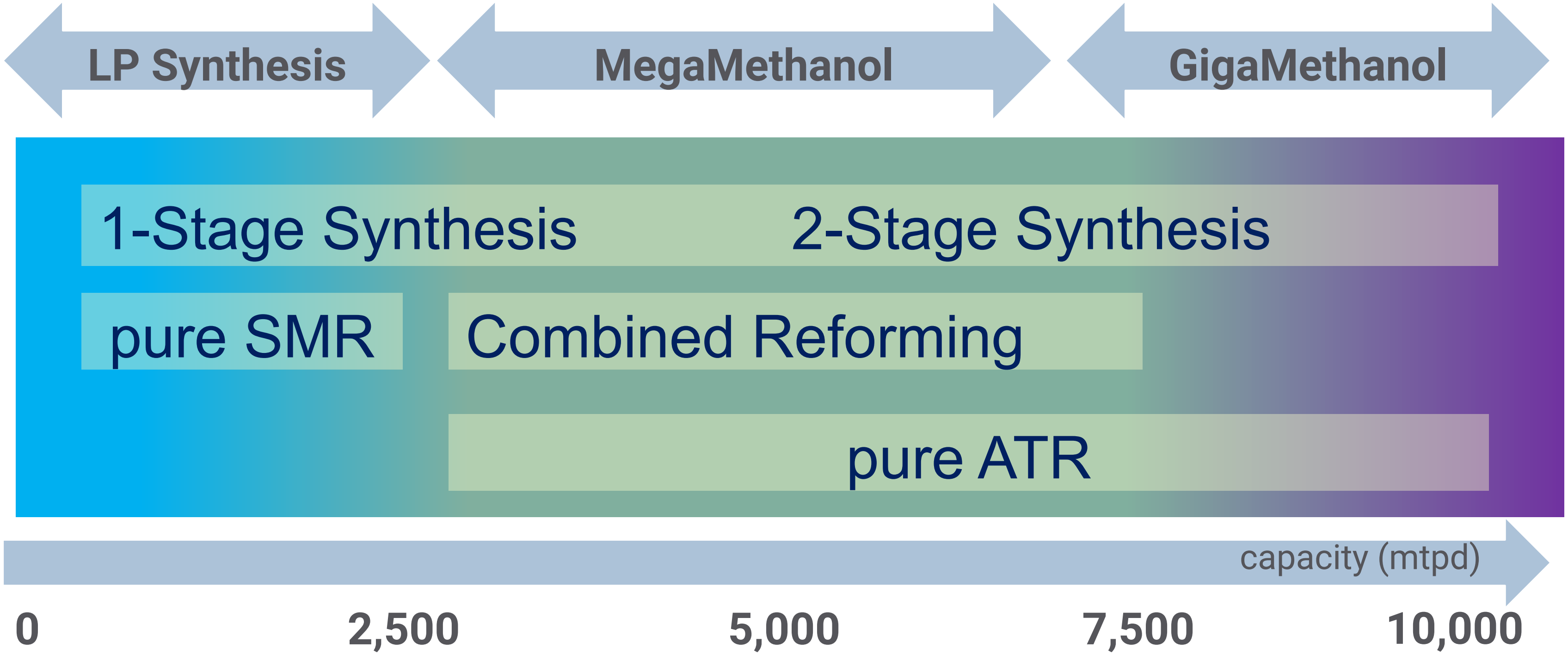
Recent Air Liquide Methanol Licenses



Lurgi MegaMethanol™: Most recent operating reference

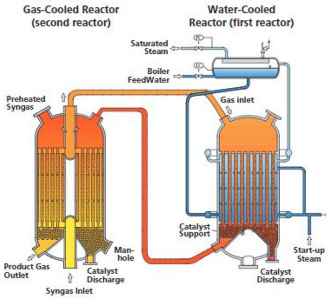
- Customer: Natgasoline LLC
- Process: Lurgi MegaMethanol™
- Licensor: Air Liquide
- Plant Capacity: 5,000 mtpd
- Feedstock: Natural Gas
- Scope of Work: L, BE, DE, Prop Eqs.
- Start-Up Year: 2018
- Project Highlights: Largest MeOH plant in the US

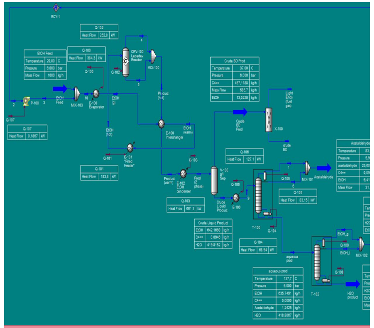
Methanol Plant concepts



Methanol Development @ AL

Methanol at Air Liquide



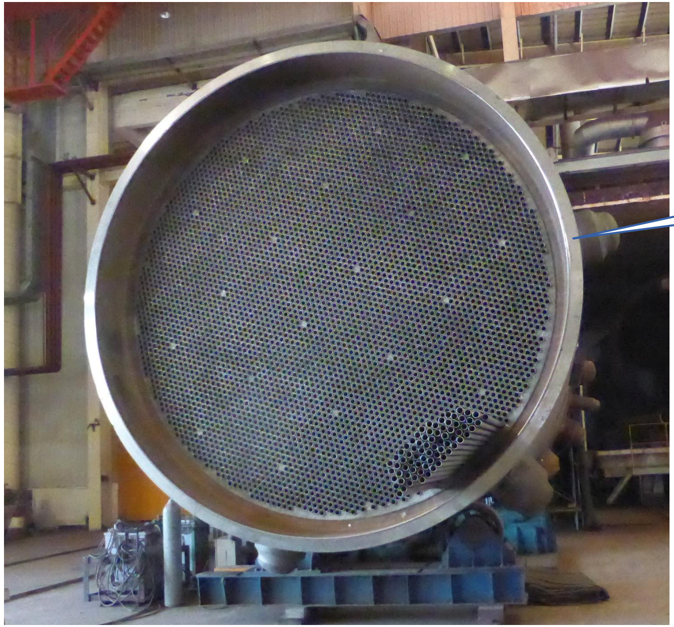


Catalyst Tests	Pilot Plants	Reactor Engineering	Modelling & Studies	Analytics
Kinetic experiments	Long-time tests	Reactor design	Kinetic models	Process analytics
Catalyst validation	Design data	Process design	Process simulation	Development of new methods
New operating conditions	Direct scale up to commercial size	Cost estimates	Economic feasibility	Support / planning for labs in plants
		Process optimization		

Methanol Process demonstration Unit (PDU311)

- Reflects different methanol loop configuration of commercial plants
- Designed for high TOS test campaign (unmanned operation (~5 days)
- All syngas composition (up to 95 bar) can be mixed
- Different process configuration (1stage synthesis, MegaMethanol design, etc.)
- Fast variation of process parameters for kinetic model training

Scale up (1stage synthesis)



Commercial world-scale reactor

4718 Tubes

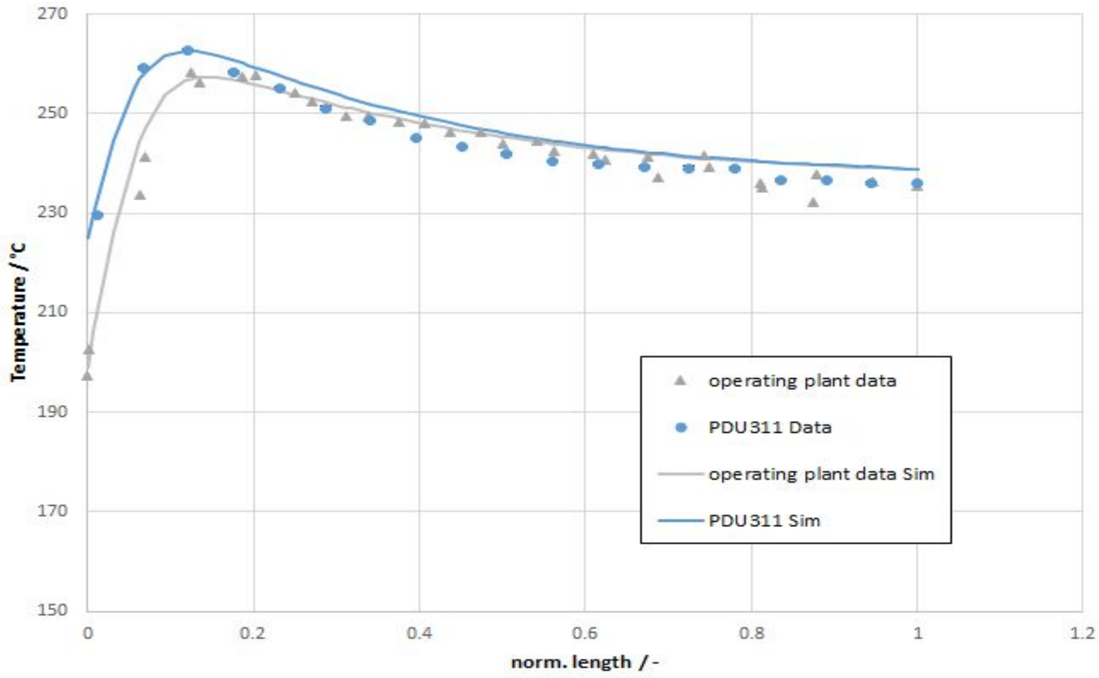
40.3 mm ID

PDU311 (R401)

1 Tubes

25.6 mm ID

Validation: PDU vs. Commercial plant



Key Data Operating Plant

- Only commercial plant that can measure detailed temperature profile
- 2000 mtpd
- Coal based
- One model for PDU and commercial plant

PDU is restricted in adjustment of inlet temperature

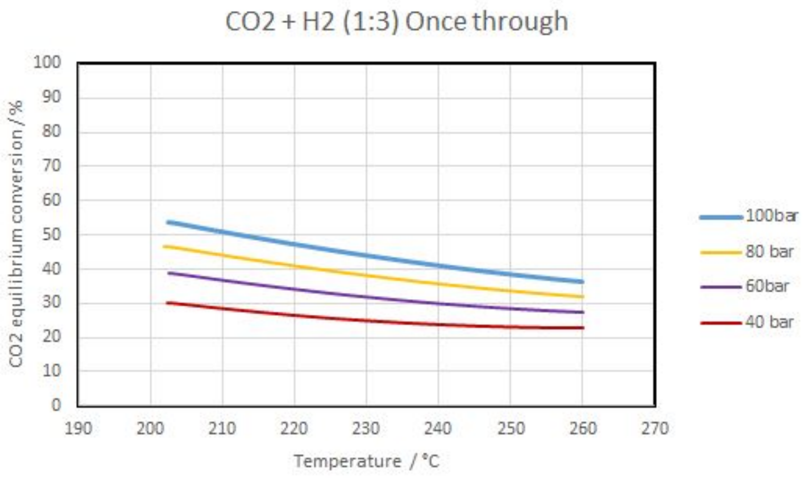
2

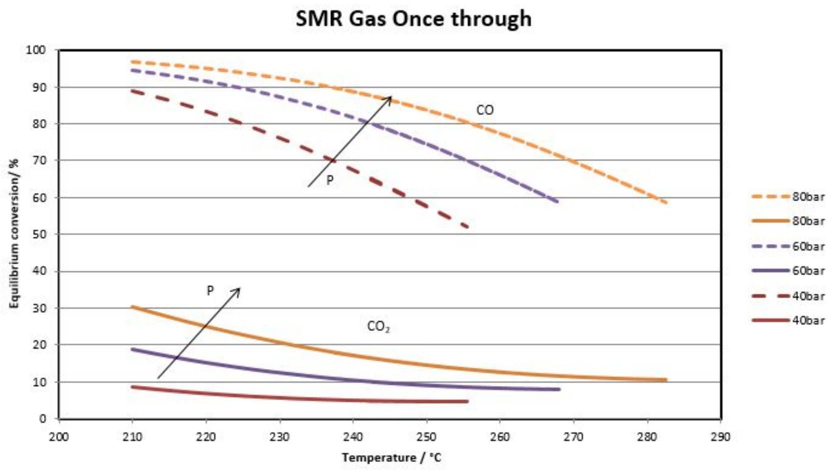
CO_2 based Methanol: Generation 1

CO_2- Based Methanol - Fundamentals: Introduction chemistry

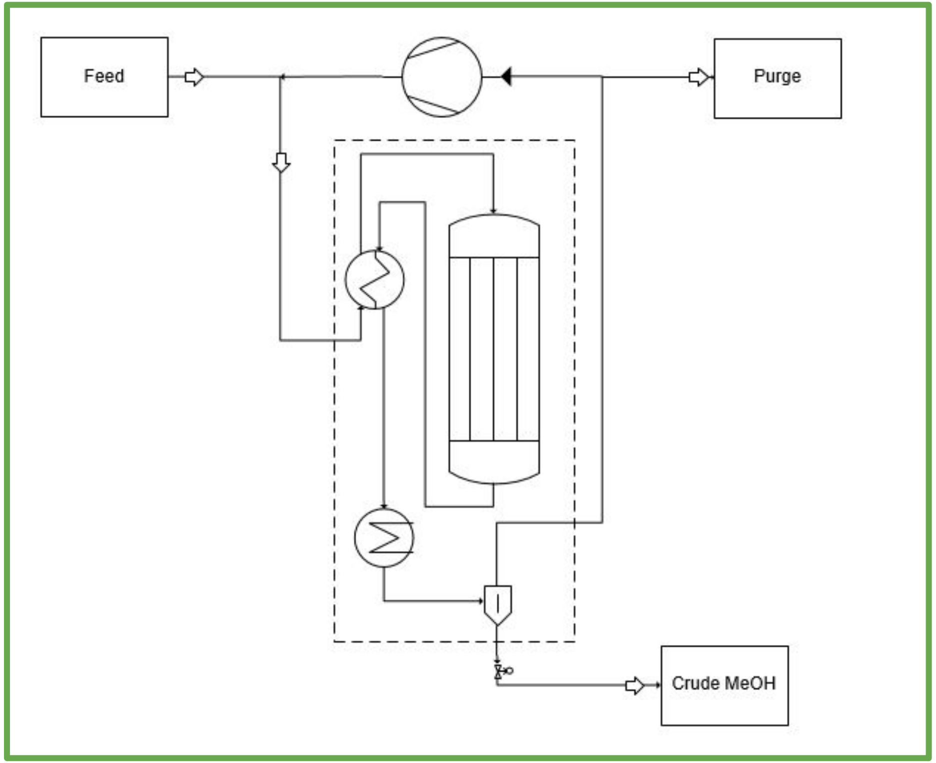
$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$
dh: -49,6 kJ/mol

$CO + 2\,H_2 \rightarrow CH_3OH$
dh -90,8 kJ/mol





CO2-to-MeOH campaign with PDU311



CO2 + H2 operational focus

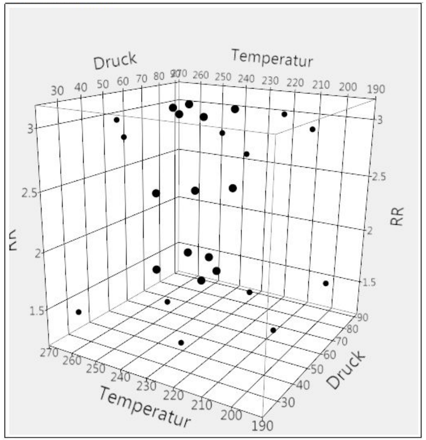
- Approx 120 kg MeOH/d on CO2
- More than 4000h TOS
- Variation of process parameters based on DoE

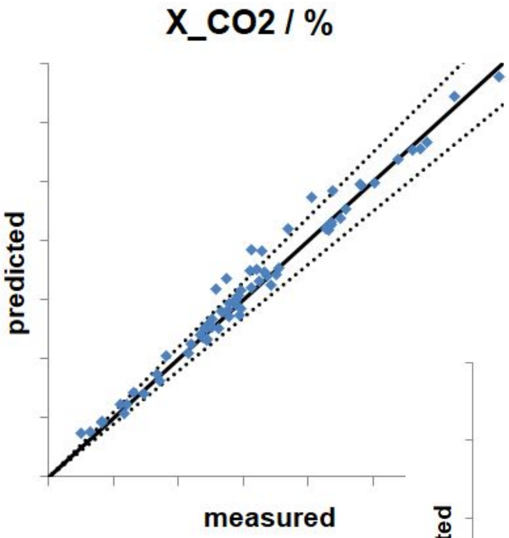
Kinetic Model training

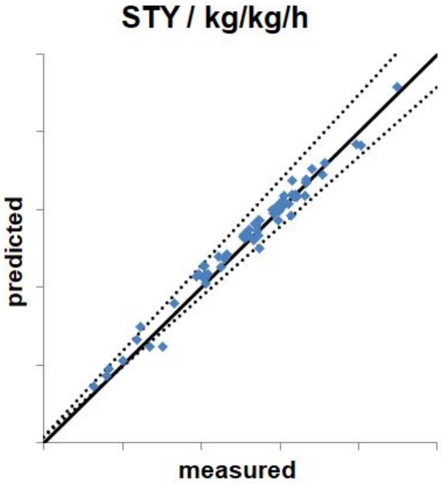
Gas Composition:

$y(CO_2)$	24,0 vol%
$y(H_2)$	74,0 vol%
$y(N_2)$	2,0 vol%
Space Velocity:	10 000 h^{-1}
Pressure	65 … 95 bar
Cooling Temperature	240 … 260 °C
Recycle Ratio	3 … 6

Design of Experiments

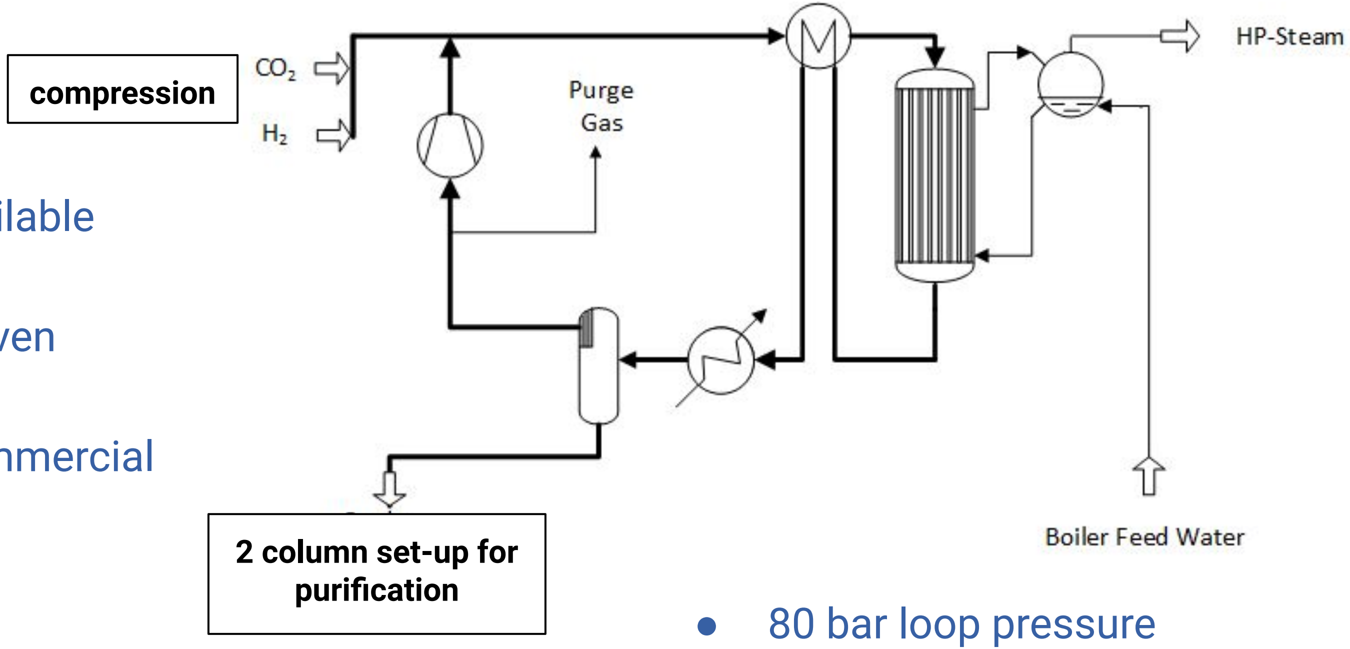






DoE provides more value of each data point.

Generation 1: Classical Loop Set-up



(+) commercially available catalyst
(+) commercially proven equipment
(+) available with commercial guarantees

- 80 bar loop pressure

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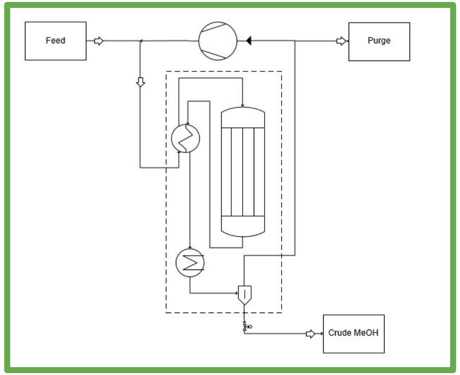
CO_2-Based Methanol: 2nd Generation

Key Process principles: **2nd Generation**

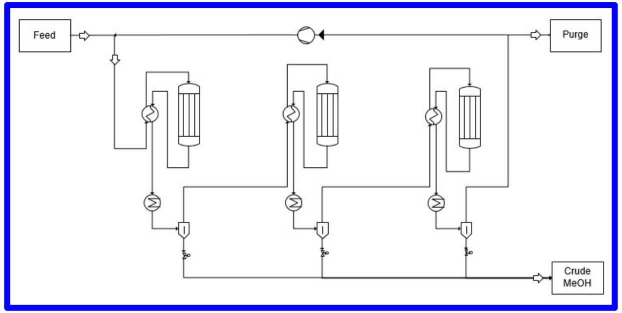
Multi-stage with inter-condensation:

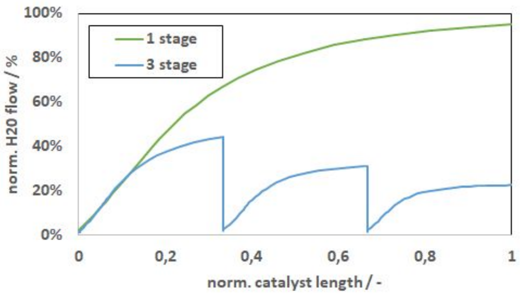
- higher (single pass) conversion
- lower gas recycle (4.5 -> 1.0)
- less H_2O flow on the catalyst
- longer lifetime (expected)
- smaller equipments
- fast adaptation to fluctuating (feed gas) conditions with...
  - ...Gas Recycle
  - ...“water/steam cooled” Reactor

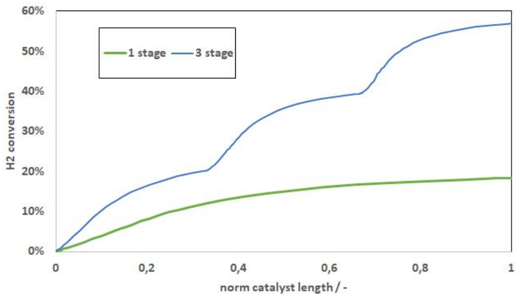
1 stage (1st generation)



3 stages (2nd generation)



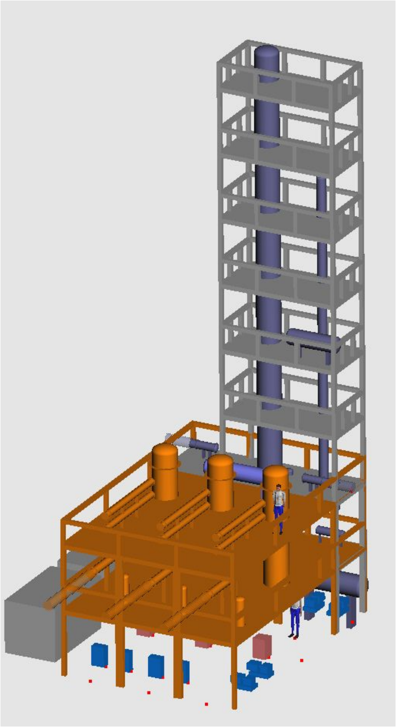




Generation 2: Multi-Stage concept

TIP last year

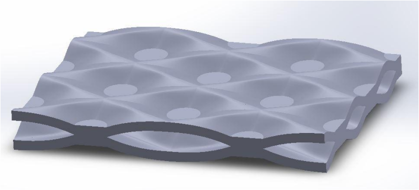
- 3 reaction stages
- Individual reactors and heat-exchangers
- Optimum process



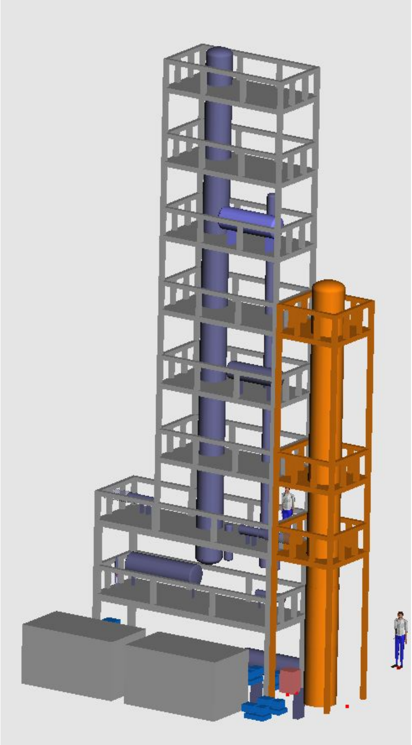
Non integrated

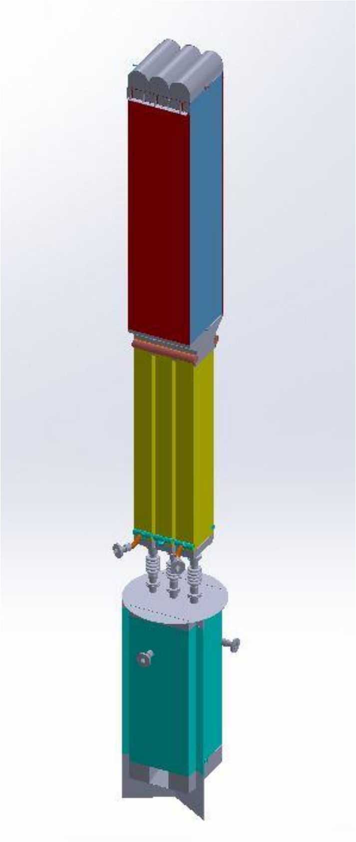
Generation 2: Integrated Multi-Stage concept

Pillow plate



process integration





(under development)

- ➥ Up to 20% lower CAPEX for synthesis section
- ➥ Up to 50% plot plan reduction

Generation II Setup

Advantages compared to Generation I:

- **Lower CAPEX due to integrated solution**
  - Higher per pass conversion -> lower recycle ratio
  - Lower equipment count
- **Small plan size → ideal for add on solutions / revamp**
- **Reduced utility consumption**

Generation I vs Generation II

1% inerts		Generation I	Generation II
Recycle ratio - Loop	-	4	1
Space time yield	kg/l/h	0.7	0.7
Hydrogen conversion	%	96	96

10% inerts		Generation I	Generation II
Recycle ratio - Loop	-	4	1
Space time yield	kg/l/h	0.55	0.45
Hydrogen conversion	%	80	90

2nd generation shows better hydrogen efficiency at increased inert content.

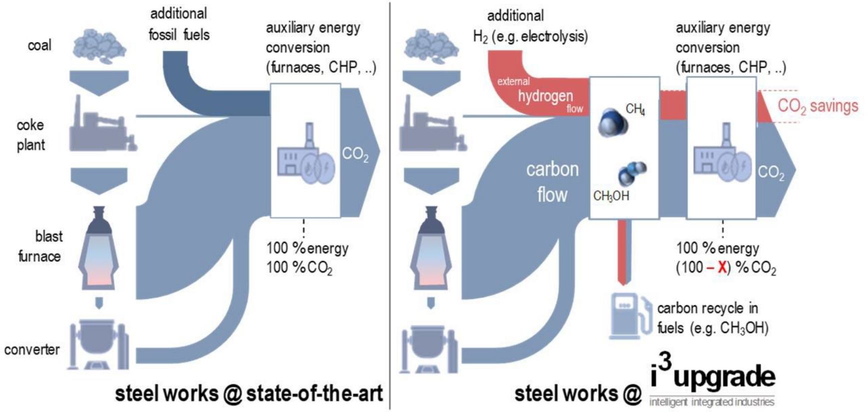
New pilot unit: i^{3}upgrade project

Key figures

- **EU Funding:** Research Fund for Coal and Steel (RFCS)
- **i³upgrade: i**ntegrated and **i**ntelligent upgrade of carbon sources through hydrogen addition for the steel **i**ndustry
- **Start:** June 2018 / **Duration:** 42 Months

Partners

Air Liquide
voestalpine ONE STEP AHEAD.
FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
K1 MET metallurgical competence center
Scuola Superiore Sant'Anna di Studi Universitari e di Perfezionamento
GIG
MONTAN UNIVERSITÄT WWW.UNILEOBEN.AC.AT
CERTH CENTRE FOR RESEARCH & TECHNOLOGY HELLAS



Website: https://www.i3upgrade.eu/

This project has received funding from the Research Fund for Coal and Steel under grant agreement No 800659

New pilot unit: start-up this month!

Process validation of 2nd generation concept (tubular basis, non-integrated)

This project has received funding from the Research Fund for Coal and Steel under grant agreement No 800659

Conclusion

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- CO2-to-MeOH process incorporates Air Liquide's long experience in Lurgi™ MeOH technology for conventional feedstocks

- 1st **Generation** available with commercial guarantees

- The **2nd Generation** CO2-to-MeOH provides you the latest and enhanced process together with the **integrated reactor** design

Air Liquide

Thank you!

You can direct further inquiries and questions to:

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