Innovative concept for methanol synthesis using unconventional gases as feedstock

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Content

- Conventional Methanol Technology
- Methanol Developments at Air Liquide
- 1st Generation CO2-to-MeOH
- 2nd Generation CO2-to-MeOH
- EU i3upgrade project: New pilot plant for valorization of off-gases from steel plant
- Conclusion

Conventional Methanol Technology

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

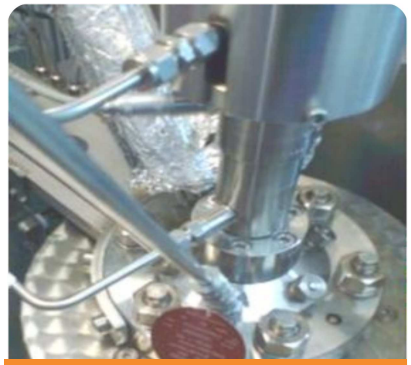
- **Different feedstocks**
  - Natural gas, naphtha, coal, residue
  - Over 60 licenses: total capacity of 49.0 MMTPY
- **Long-standing cooperation with** CLARIANT
- **Full service portfolio**
  - Licensing + proprietary design
  - Basic + detailed engineering design
  - Construction + commissioning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

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 Development @ AL

Methanol at Air Liquide



Catalyst Tests

Kinetic experiments

Catalyst validation

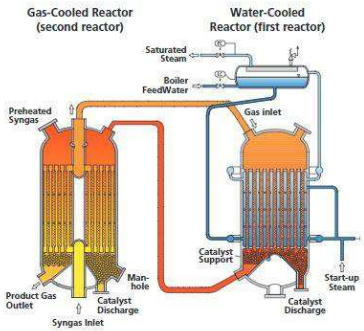
New operating conditions

Pilot Plants

Long-time tests

Design data

Direct scale up to commercial size



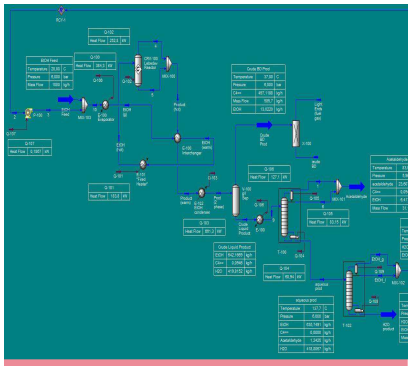
Reactor Engineering

Reactor design

Process design

Cost estimates

Process optimization



Modelling & Studies

Kinetic models

Process simulation

Economic feasibility

Analytics

Process analytics

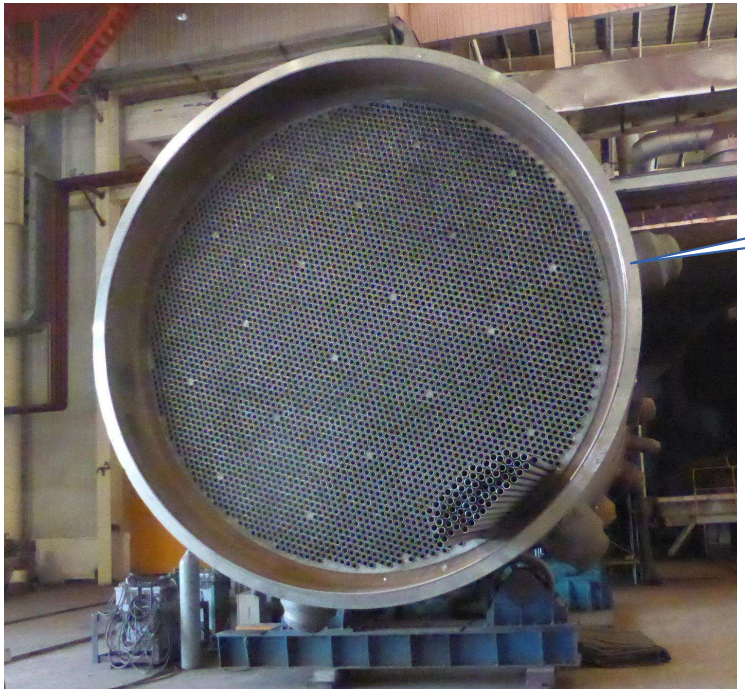
Development of new methods

Support / planning for labs in plants

Methanol Pilot Plant (in operation since 2007)

- Reflects different methanol loop configuration of commercial plants
- Designed for high TOS test campaign (24/7 operation)
- 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

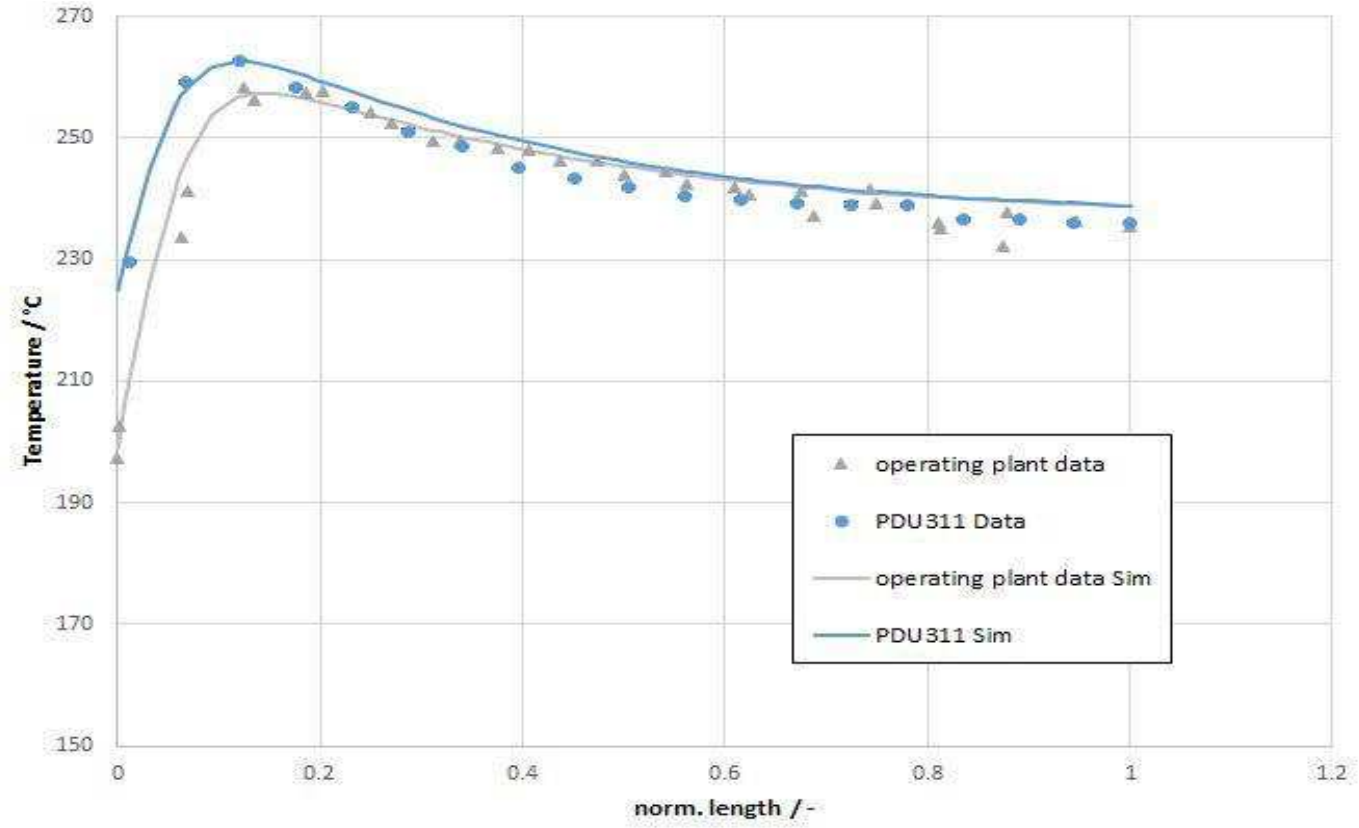
Scale up (1stage synthesis)



Commercial world-scale reactor
4718 Tubes
40.3 mm ID

Pilot Plant
1 Tube
25.6 mm ID

Validation: Pilot plant vs. Commercial plant



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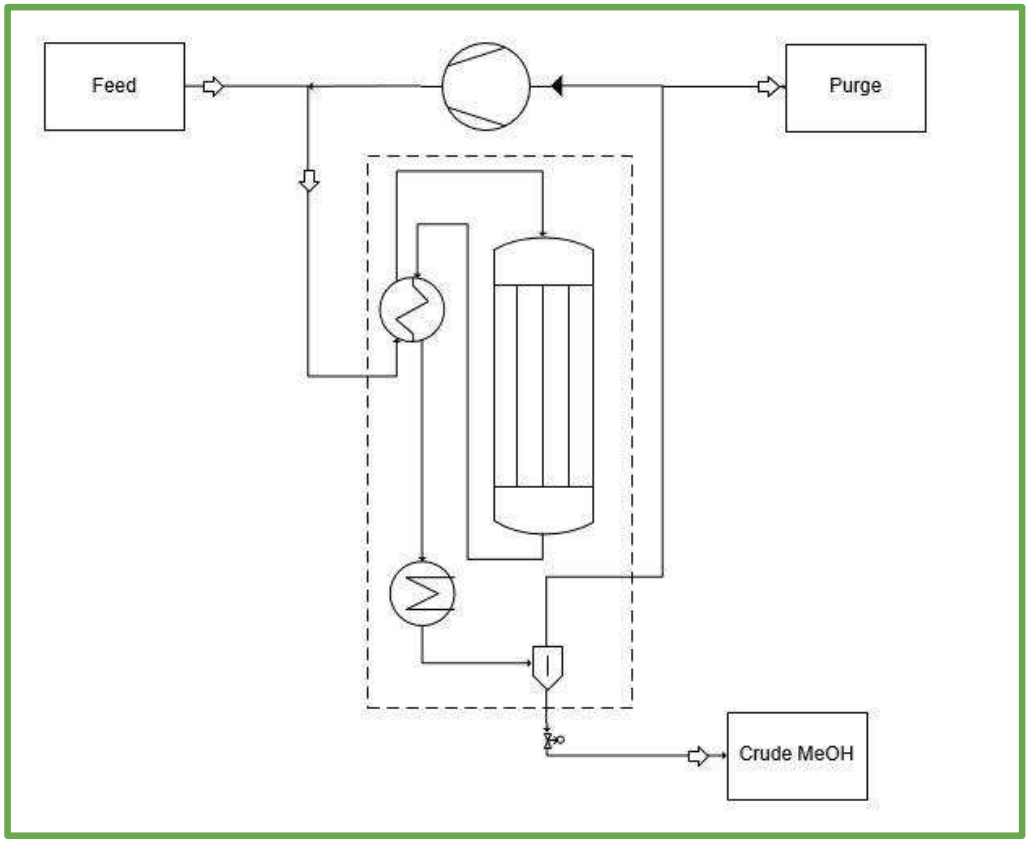
CO_2 based Methanol: Generation 1

CO2-to-MeOH campaign



CO2 + H2 operational focus

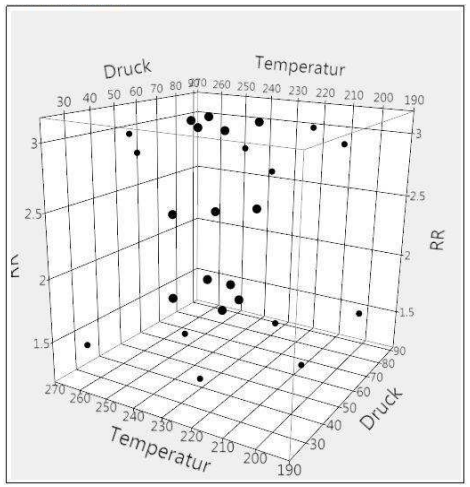
- Approx 120 kg MeOH/d on CO2
- More than 4000 h TOS
- Variation of process parameters based on DoE

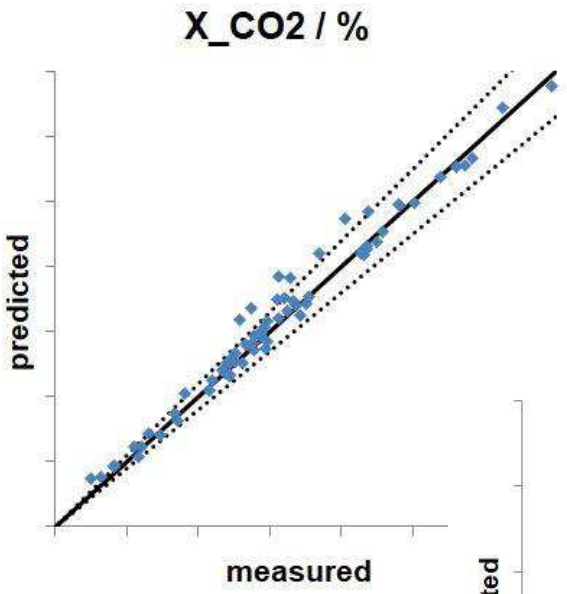
Kinetic Model training

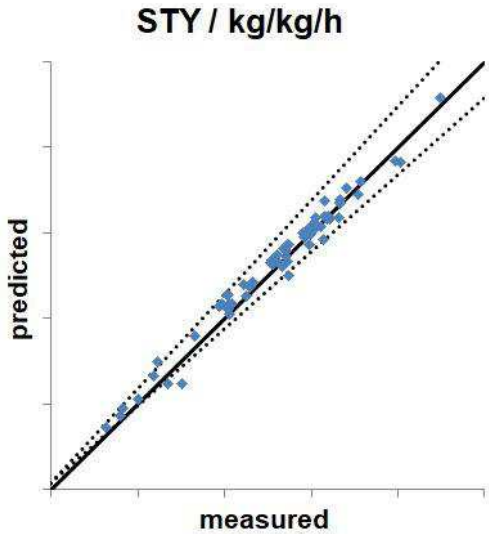
Gas Composition:

$y(CO_2)$	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



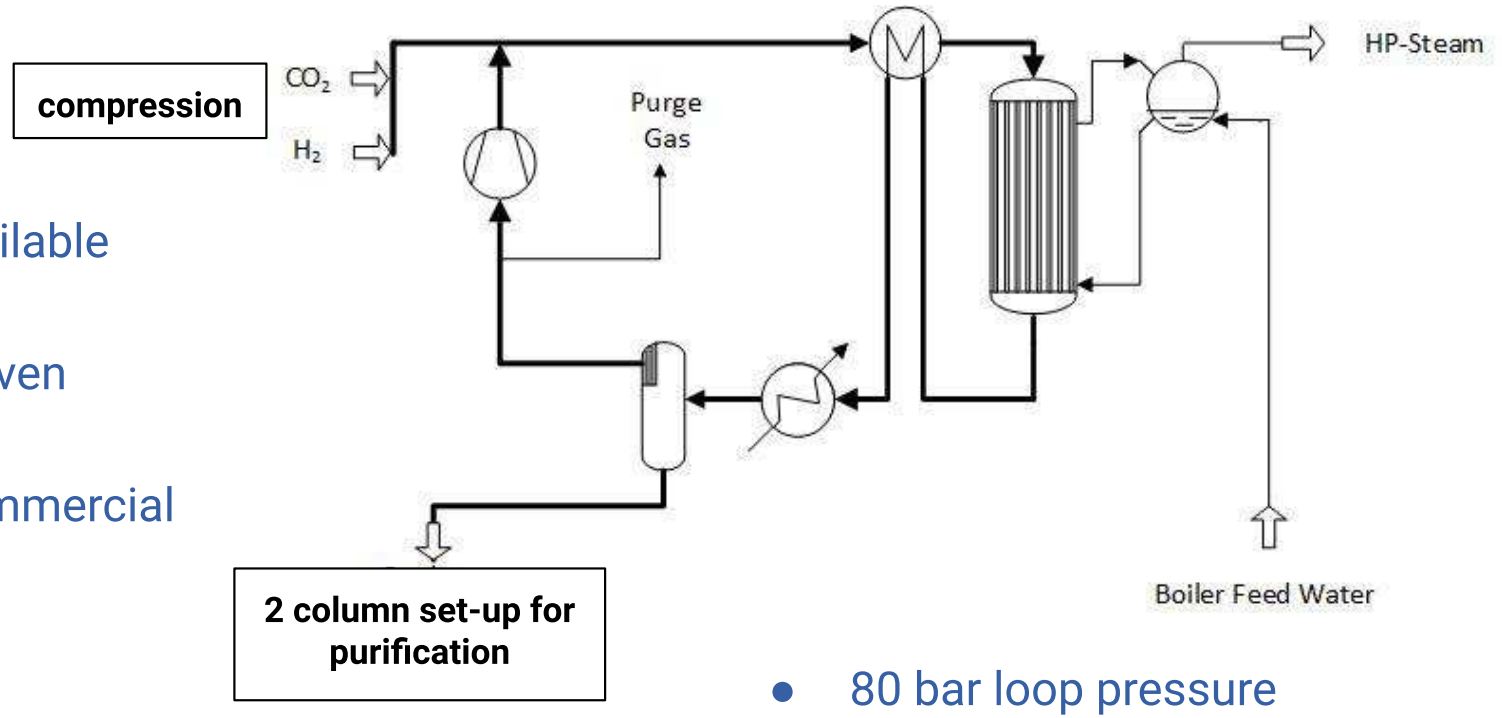




DoE provides more value of each data point.

Generation 1: Classical Loop Set-up

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



- 80 bar loop pressure

3

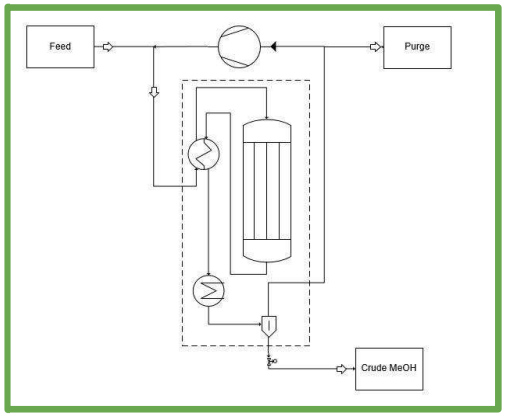
CO_2-Based Methanol: 2nd Generation

Key Process principles: **2nd Generation**

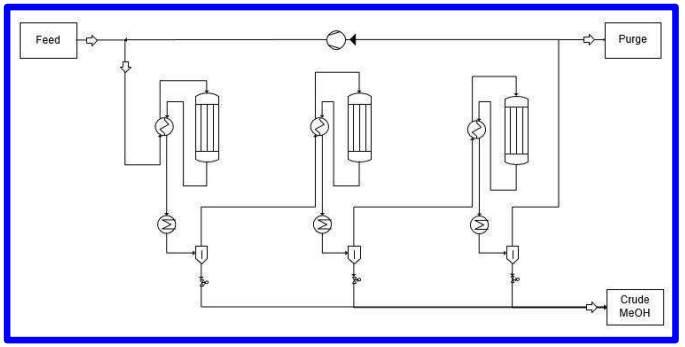
Multi-stage with inter-condensation:

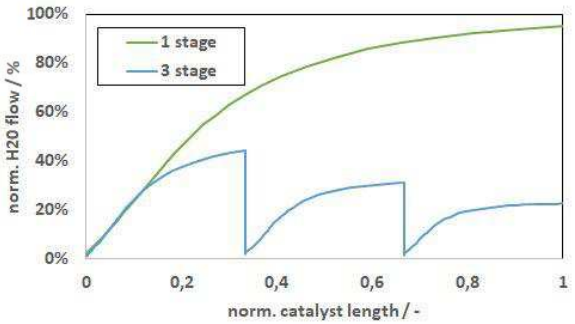
- higher (single pass) conversion
- lower gas recycle (4.5 -> 1.0 or lower)
- less H_2O flow on the catalyst
- longer lifetime (expected)
- smaller equipments
- fast adaptation to fluctuating (feed gas) conditions with...
  - ...Gas Recycle
  - ..."water/steam cooled" Reactor

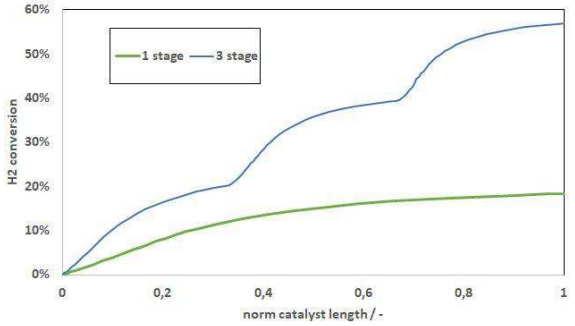
1 stage (1st generation)



3 stages (2nd generation)

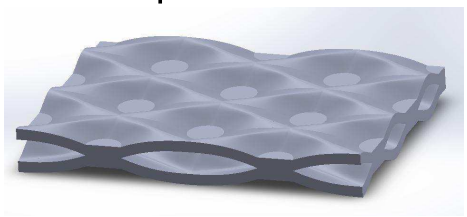




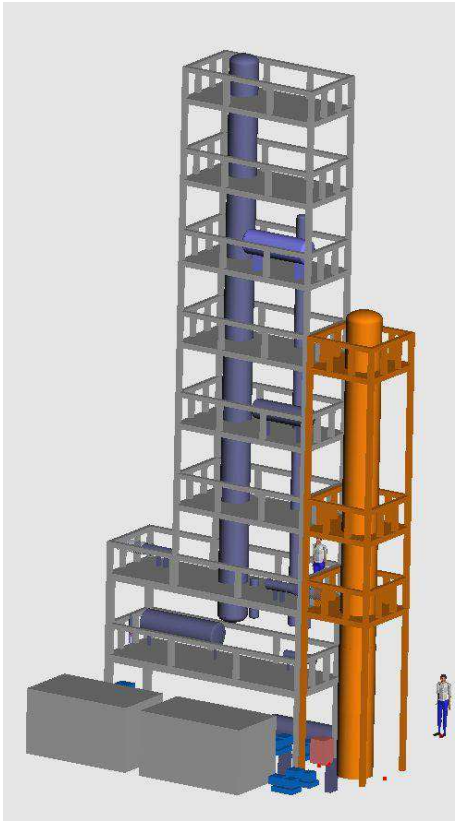


Generation 2: Integrated Multi-Stage concept

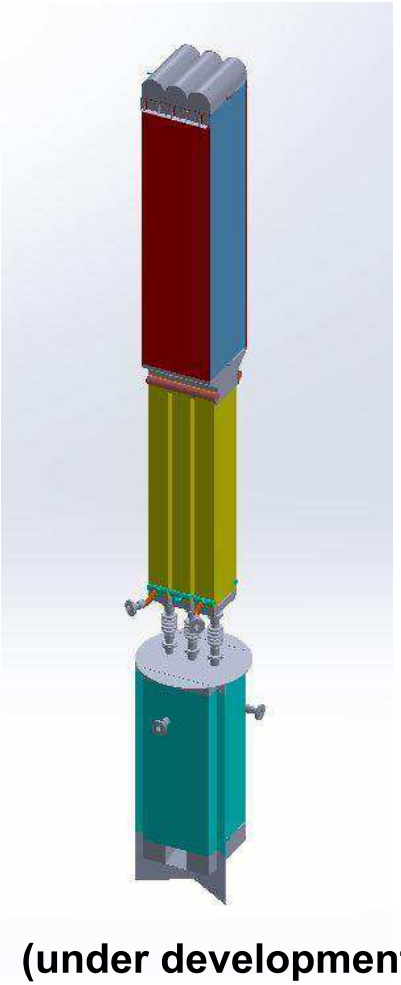
Pillow plate



process integration



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



(under development)

Generation I vs Generation II

1% inerts		Generation I	Generation II (as example with 3 stages)
Recycle ratio - Loop	-	4	1
Space time yield	kg/l/h	0.7	0.7
Hydrogen conversion	%	96	96

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 plant size → ideal for add on solutions / revamp**
- **Reduced utility consumption**
- **Expected longer catalyst lifetime**

4

EU i3upgrade project: New pilot plant for valorization of off-gases from steel plant

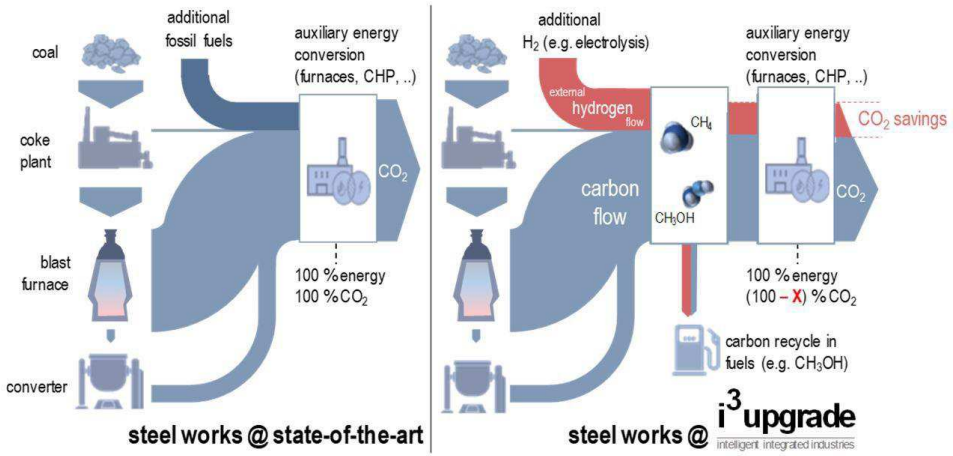
i3upgrade project

Key figures

- **EU Funding:** Research Fund for Coal and Steel (RFCS)
- **i³upgrade:** integrated and intelligent upgrade of carbon sources through hydrogen addition for the steel industry
- **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
CERTH CENTRE FOR RESEARCH & TECHNOLOGY HELLAS
GIG
MONTAN UNIVERSITÄT WWW.UNILEOBEN.AC.AT



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 built in the frame of i3upgrade

Process validation of multi-stage concept (tubular basis, non-integrated)

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

New pilot built in the frame of i3upgrade

- Reactor with tubes
- Several reactor stages
- Various flow schemes possible
- Heat transfer to steam system
- Temperature profile measurement
- Throughput:
  - Feed gas up to 35 m^3_N/h
  - Raw methanol product up to 20 kg/h

- Comprehensive control & automation devices:
  - 178 Temperature
  - 70 Pressure
  - 29 Flow
  - 9 Level
  - 6 others
- Analysis points:
  - Hot gas sampling (preferred)
  - 11 for gases (online)
  - 5 for liquids (offline)

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First test campaign without recycling

Typical Blast Furnace Gas composition + additional H2 (adjusted SN to 1.5)

- Composition: **12.1v%CO2, 12.9v%CO, 49.9v%H2, 25.1v%N2**
- High amount of nitrogen!
- Low stoichiometric number (low amount of hydrogen)!
- **4 stages filled with catalysts**
- **Interstage condensation & separation**
- **Once-through operation**
- Different pressure: 50, 70, 90, 110 bar
- Different load: 6.7 Nm³/h, 11.2 Nm³/h, 15.8 Nm³/h

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First test campaign without recycling

P bar	**MUG** Nm³/h	**X_CO2** plant	**X_CO** plant	**X_H2** plant
50	6.7	33.2%	88.4%	63.6%
70	6.7	39.1%	93.3%	72.7%
70	11.2	37.3%	92.2%	70.6%
90	6.7	45.0%	95.4%	78.1%
90	11.2	43.8%	94.9%	76.6%
90	15.8	42.8%	94.1%	74.4%
110	6.7	49.3%	96.5%	81.9%

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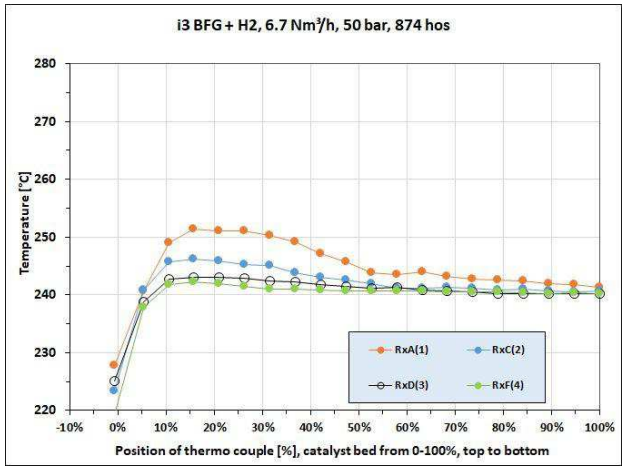
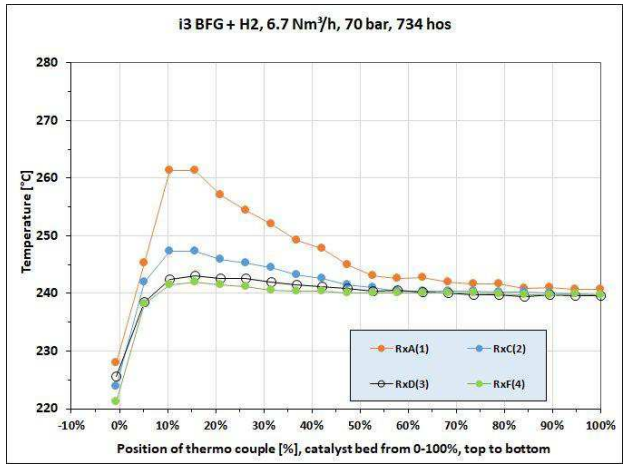
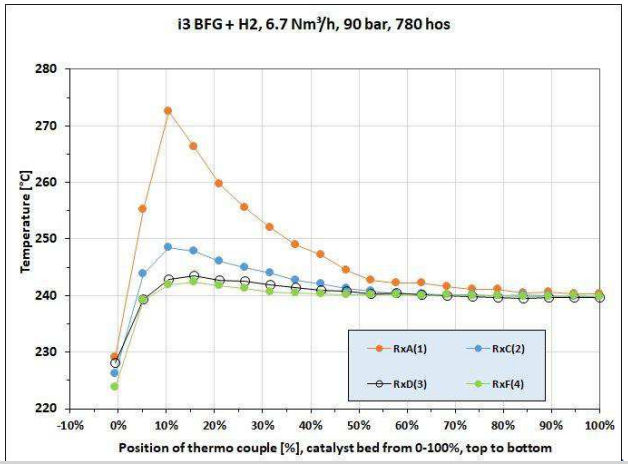
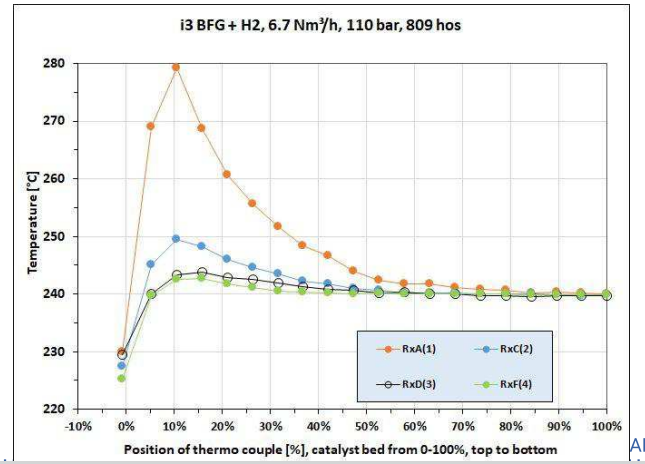
First test campaign without recycling









P bar	MUG Nm³/h	Tota by-products wt-ppm
50	6.7	3808
70	6.7	3928
90	6.7	3909
110	6.7	3548

By-products formation is in a good range for the distillation section even by fluctuating operation and fluctuating Tmax in the first stage!

AND SERVICES FOR INDUSTRY AND HEALTH

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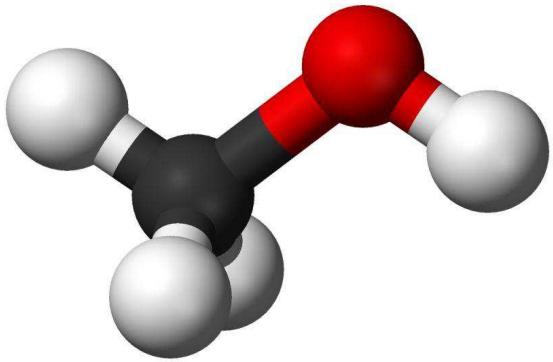
Conclusion

- **CO2-to-MeOH process:**
  - incorporates **Air Liquide's long experience in Lurgi™ MeOH technology** for conventional feedstocks
  - **1st Generation** CO2-to-MeOH available with **commercial guarantees**
  - The **2nd Generation** CO2-to-MeOH provides you the latest and enhanced process together with the **integrated reactor design**
- **New pilot plant at AL R&D:**
  - **Successfully started** (already more than 1000 h-o-s in operation)
  - Will support **new developments in CO2-to-MeOH and in valorization of off-gases from industries**
  - Possible use of **hydrogen produced by an electrolyzer** in the near future

Thank you very much!

Any Questions ?



Air Liquide

You can direct further inquiries and questions to:

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Methanol from CO2