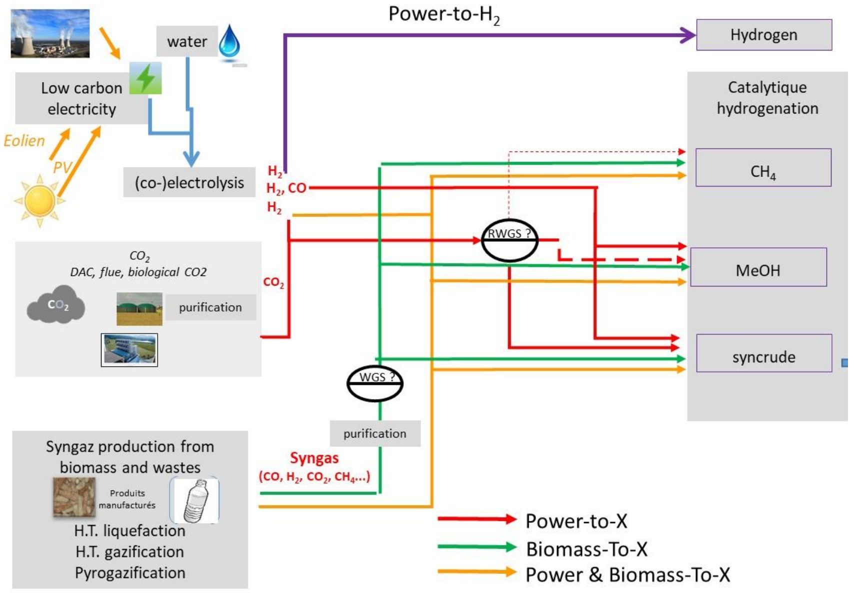
Millistructured Heat Exchangers Reactors for Power to X applications

G.Geffraye

Advanced Power-to-Gas and Power-to-Liquids Technologies (e-fuels)

8-9 march 2021

Context of thermocatalytic conversion component development



Thermocatalytic conversion

Inlet gases : CO_2, CO, H_2, other

Catalyst

Identification of active catalyst
Determination of operating conditions
Kinetic modelling
Characterization and long term behavior

Reaction specificity

Exothermal / Endothermal
Equilibrium / Total conversion
Selective / not selective
Direct / Indirect pathway

Reactor

Multiphysic modelling of reactor behavior
Design proposal
Experimental validation
Upscaling proposal

Products : CH_4, MeOH, olefins, syncrude
(+ Specs)

Reactors developments : case of methane synthesis

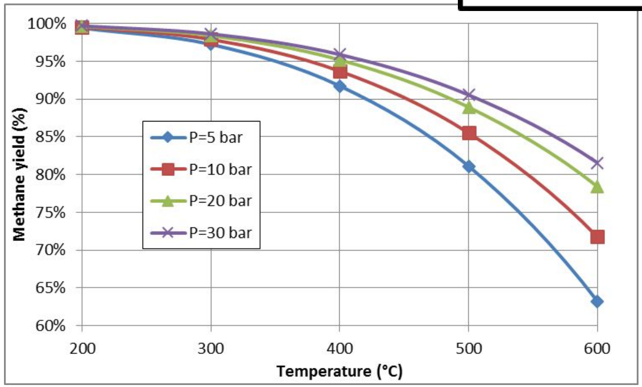
Reactors developments for liquid production

Reactor developments for PtG : Thermodynamics and catalyst activity

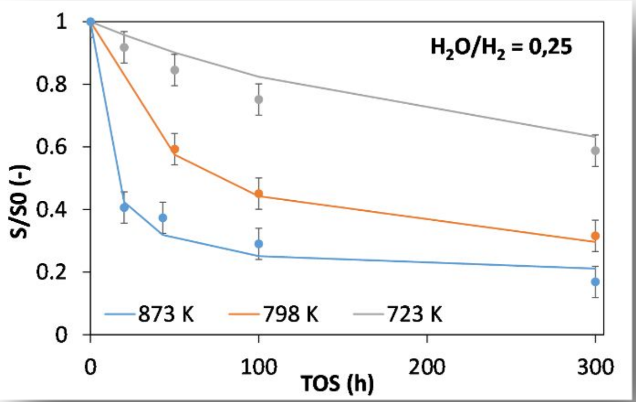
Sabatier reaction : $CO_2 + 4H_2 \Leftrightarrow 2H_2O + CH_4 \quad (\Delta_r H_{298} = -165 KJ/mol)$

$$Y_{CH4} = \frac{F_{CH4,outlet}}{F_{CO_2,inlet}}$$

- ✔ Equilibrated, highly exothermic, and catalyzed by metals
- ✔ Thermodynamics favored at low temperature
  Yield > 97% for T<300°C
- ✔ Catalyst activity favored at high temperature



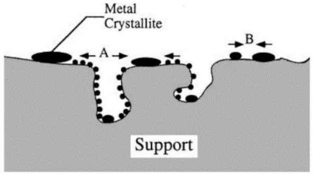
Methane yield calculated by Gibbs energy minimization for H_2:CO_2 = 4:1

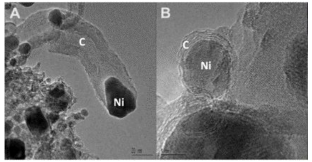


Ni surface (TPD) time evolution at 3 temperatures

Isabelle Champon, NGCS 12, San Antonio, 3rd of June 2019

- ✔ Deactivation mechanisms favored at high temperature
  Poisoning, carbon deposition, thermal degradation, attrition, crushing





C.H.Barthomew. Applied Catalysis A: General 2001 212 17.

Reactor developments for PtG : SoA

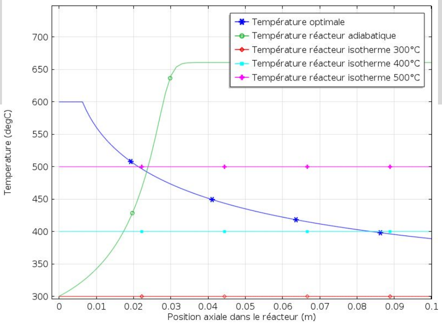
Temperature management issue :

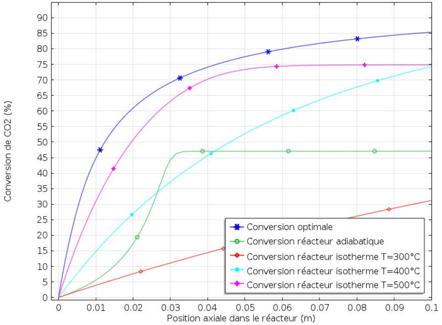
- High enough to promote the reaction kinetics
- Low enough to favor thermodynamics (conversion, selectivity)
- Outside of critical ageing temperature ranges (thermal ageing and volatilization) to reach acceptable catalyst lifetime

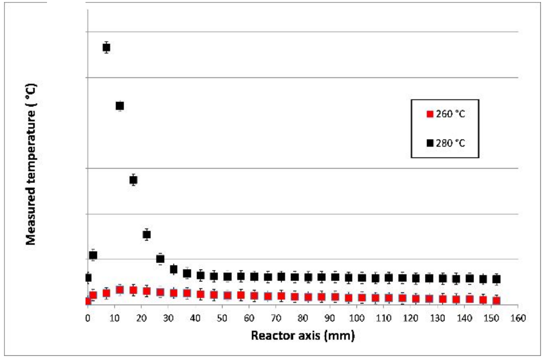
	Adiabatic fixed-bed	Cooled fixed-bed	Fluidized bed	3 phase reactors	Micro-reactor	Monolith	Milli-structured
Operation mode	Adiabatic	Polytropic	Isothermal	Isothermal	Polytropic	Polytropic	Polytropic
Process complexity	High	Low	Low	Low	Low	Low	Low
Catalyst	Packing	Packing	Fluidized	Fludized or suspended	Coated	Coated	Packing
Particle size	Millimeters	Millimeters	100-500 µm	< 100 µm	<200 µm	< 100µm	< 1 mm
GHSV	Medium-high	High	Low	Low-medium	Very high	Very high	High
TRL	9	7	7	4-5	4-5	4-5	5-6

Modified from Catalytic reactors classification based on hot spot temperature

S. Rönsch, Fuel 166 (2016) 276–296



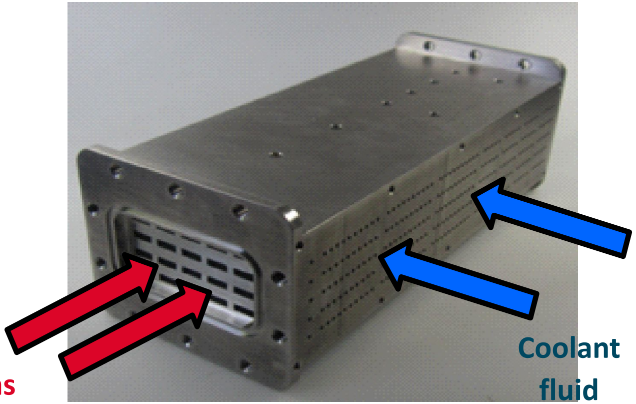




✔ Enhancement of temperature control
✔ Compacity & Modularity
✔ High conversion rate

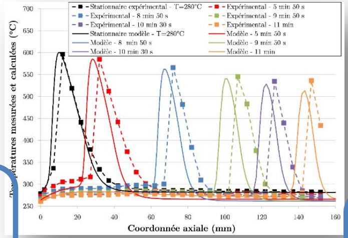
- Millimetric reaction channels (<cm)
  - *intensification of heat and mass transfer*
- Millimeter-scale catalyst particles
  - *high catalyst density and easy loading*
- Intensification cross flow cooling with a thermal liquid

- Compactness
- Safety : coolant organic oils
- Modular concept (easy scale-up by numbering-up reactive channels and coolant channels)
- Easy maintenance



Reactor developments for PtG : Methodology

Reactor shut-down : 280-260°C, VVH 15600 h^{-1}, H_2/CO_2 ratio 4, P = 2.5 bar [25]
Rasmey Try, PhD Thesis, Université de Lyon, 2015



Selected catalyst

Ni-Al2O3

Highly instrumented HX reactor

Catalyst and reactor characterisation

Design tools and detailed analysis

Gas lines:
Ar, CO_2, CO, H_2, CH_4, H_2O

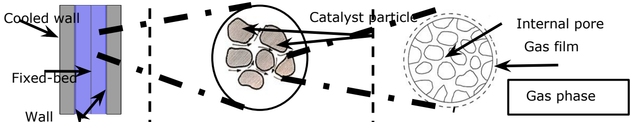
Pressure: 1-20 bars
Temperature: 20-350°C
Total Q : up to 15Nm³/h

Wide range of inlet gas composition

Catalyst analysis :
Evolution of physico-chemical properties

Instrumentation: T(°C)
profile along reactor

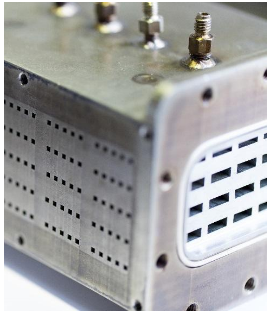
Gas Analysis (μ-GC) :
CO_2, CO, H_2, CH_4



Reactor scale:
- Macroscopic heat, mass and momentum transfer
- Wall heat transfer

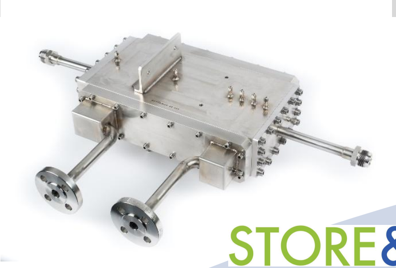
Bed scale :
- Heat, mass and momentum transfer around the catalyst
- Gas-particle heat and mass exchange

Catalyst particle scale :
- Heat and mass transfer in the particle
- Kinetics
- Heat release by the reaction



☐ Towards an optimized reactor design and sizing

Reactor developments for PtG: Reactor roadmaps



STORE&GO

KHIMOD ALCEN

Industrialization (partner)

Demonstration (with partner)

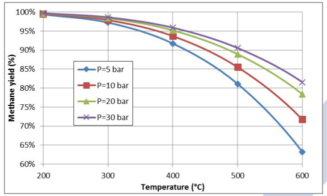
Proof of Concept Labscale

Technology selection

Reactors Performance tests : up to 12,5 Nm3/h et 15 bars : Ar, H_2, CO, CO_2, CH_4

About ~3 Nm3/h & 80 bar : Ar, H2, CO, CO2, CH4

Catalyst Ageing Facility : ~0,2 Nm3/h & 80 bar : Ar, H2, CO2, CH4

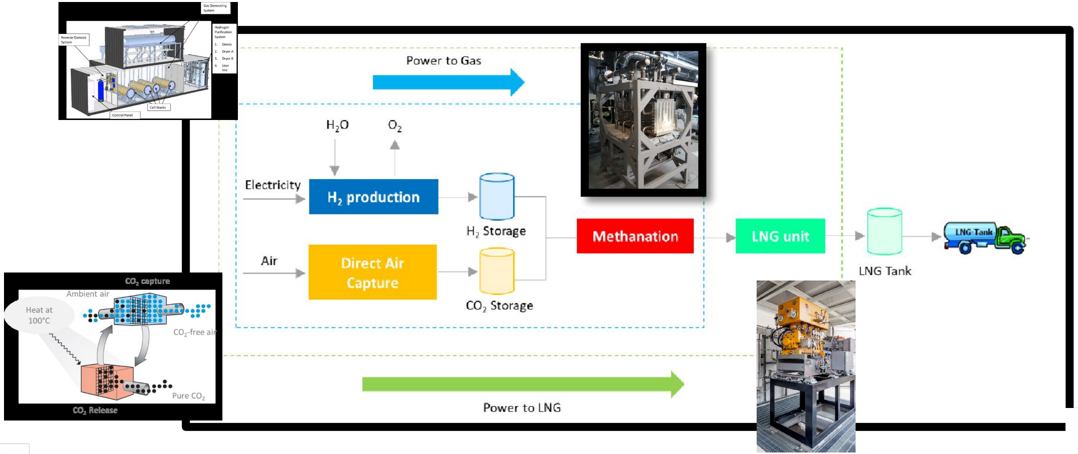


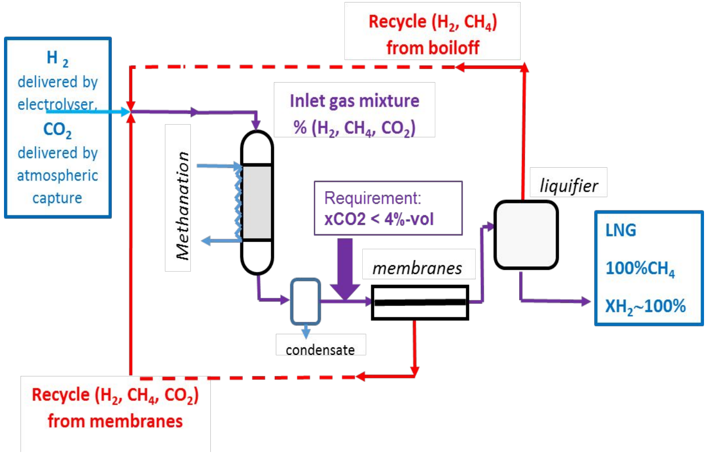
R&D and technological survey

Reactor developments for PtG: Example of STORE&GO project (TROIA demo)

KHIMOD ALCEN

STORE&GO





- Requirement to have < 4%-vol CO_2 at the reactor outlet
  - High conversion rate > 95%
- Methanation reactor integrated in a recycling system
  - Impact on the inlet gas compositions possible presence of CH_4, possible H_2/CO_2>4, different % ($H_2/CO_2/CH_4$)
- Thermal management optimisation
  - to limit temperature increase (<500°C) to prevent catalyst ageing (4000h)

Reactor developments for PtG: STORE&GO methanation reaction development

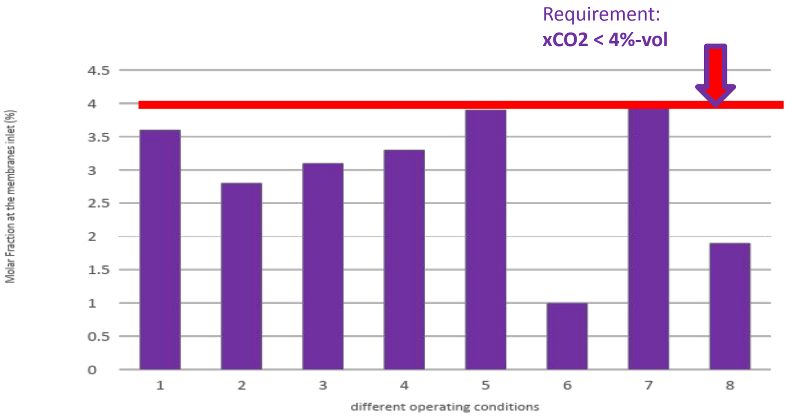
Manufacturing and test a one stage module of 0.8m3/h (NTP) reactor

- Design based on numerical simulations, experimental analysis, and taking into account the manufacturing experience

Dimensions (Length x Width x Thickness): ~100 x 400 x 200 mm.

manufactured by KHIMOD

- A large Matrix of labscale tests at CEA to:
  - Support the design of the full scale geometry
  - Guide the definition of optimal operation points of the methanation unit.



case	Pressure Bar	2 zones T °C	Ratio H2/CO2	CH4 % vol
1	6	280-310	4	5
2	4	290-310	4,1	6
3	4	290-310	4,1	0
4	4	280-310	4.1	0
5	4	280-310	4	6
6	2,5	290-290	4.5	0
7	2,5	290-310	4,1	0
8	2,5	280-280	4,5	0

Reactor developments for PtG: STORE&GO methanation unit in TROIA

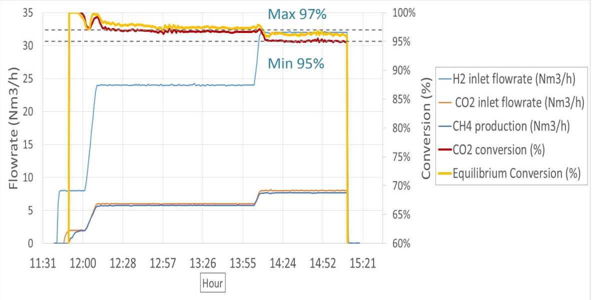
Fully integrated unit in two 20’ containers.

4 Heat Exchangers Reactors

H2 inlet flow : 8 to 40 Nm3/h (with recycle)

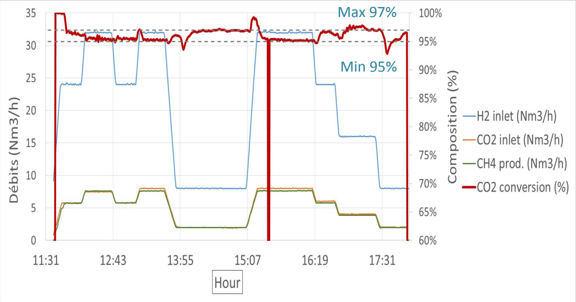
CO2 inlet flow : 2 to 10 Nm3/h (with recycle)

All data and figures are from KHIMOD ALCEN



Conversion performances :

- Close to thermodynamic equilibrium maintained over a wide range of flow rates (H_2 from 8 to 32 Nm3/h & without recycle)
- Conversion above 95% without recycle.

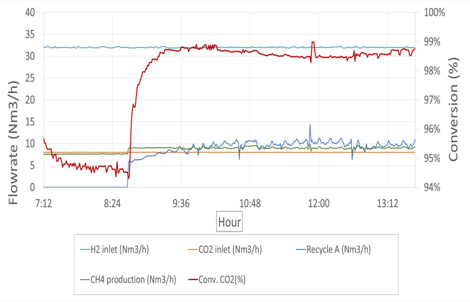


Flexibility of methane production to fit the fluctuation of CO_2 or renewable electricity :

Fast response time of the overall methanation unit under 5 to 10 minutes.

Despite of the load variations, keep the same :

- High level of conversion ratio.
- Output gas composition



Recycle capacity of the methanation unit increases methane production increasing significantly the conversion of CO_2 thanks to the recycle of H_2.

- CO_2 conversion rises from 94% to **99%**
- Unconverted H_2 is recycled and finally completely converted into methane
- The methane outlet produced is compliant to the LNG production (%CO_2 <0.5%)

Reactors developments : case of methane synthesis

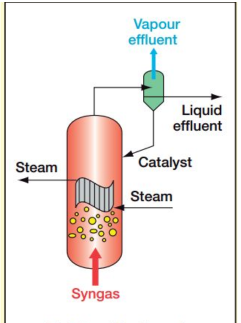
Reactors developments for liquid production

Reactor developments for syncrude production: SoA

Cata = Fe,Co T ≈ 200°C-350°C, P ≈ 20 bars

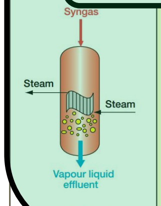
$$n\,CO + (2n+1)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O$$

Fluidised bed	Fixed bed	Slurry
Better thermal control	Better poisonning resistance	Better thermal control
Sensivity towards liquid α < 0,7	*A priori* less thermal control	Mechanical stress
Cata = Fe T > 290°C (α = 0,7) Main pdct = gasoline	Cata = Co ou Fe T < 250°C (α = 0,9) Main pdct = diesel	Cata = Co ou Fe T < 250°C (α > 0,9) Main pdct = diesel
Low compacity	High compacity	Intermediate compacity



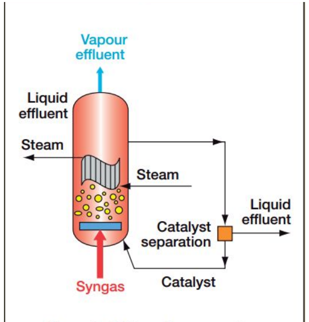
Fluidised-bed reactor

Technologies:
- Sasol SAS (FFB)
- Sasol synthol (CFB)



Fixed-bed reactor

Technologies:
- Shell SMDS
- BP



Slurry bubble column reactor

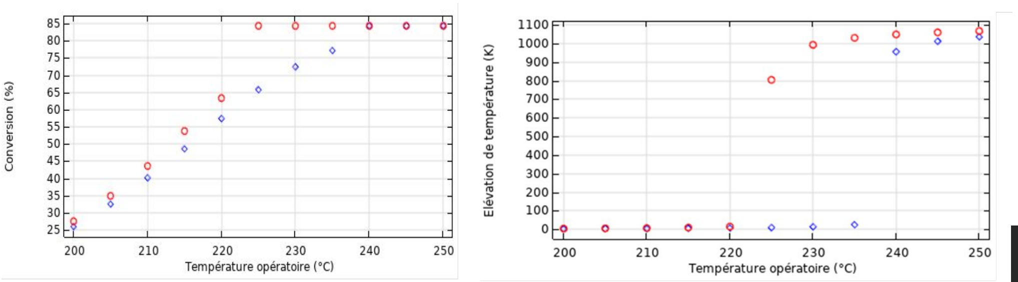
Technologies:
- Sasol SPD
- ExxonMobil AGC–21
- Eni/IFP/Axens Gasel
- Statoil (GTL. F1)
- ConocoPhillips

Reactor developments for syncrude production : Millistructured FT reactor sizing

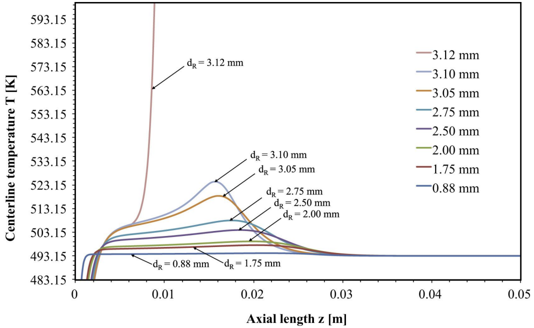
Chabot G. & al, Chemical Engineering Science, 2015

FT reactor design based on bibliography, preliminary simulations (*) and first experimental tests ‘low’ channel height to

✔ Limit the rise in temperature and preventing the aging of the catalysts

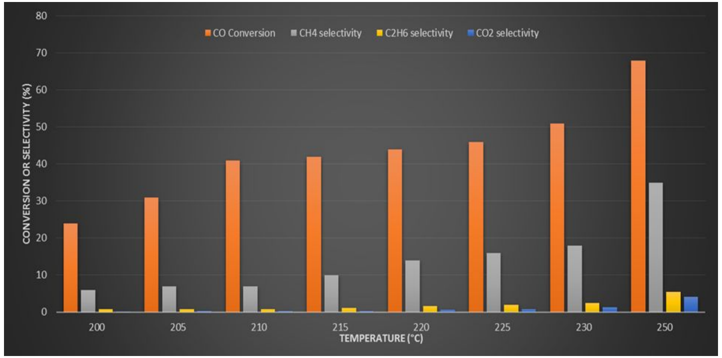


Evolution of the maximum increase temperature &conversion function of temperature for two channels height (red=blue+1mm)



Influence of the reaction channel diameter on the temperature along axial direction

✔ Ensure a better selectivity towards the desired products



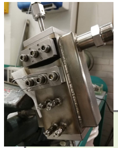
Temperature sensitivity of the coolant and the inlet gases (H2 /CO)
Evolution of CO conversion and selectivities to methane and ethane

(*)Specificities for simulation:

- Multiphysics
- Triphasic system (gas-liquid-solid)
- Innovative catalyst => few data available (no kinetics, thermal properties …)

Reactor developments for syncrude production : Example of Heat to Fuel project

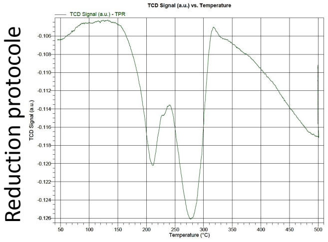
1rst Modeling and simulation



Prototype
Small scale reactor
(0,1 Nm^3/h)
Several candidate catalysts

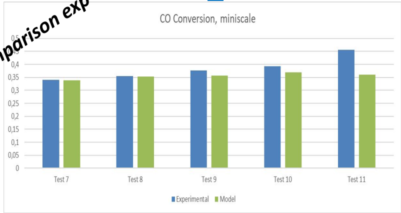
1rst Tests

Catalyst selection



Temperature programmed reduction (TPR)

comparison exp-model



Improved modeling

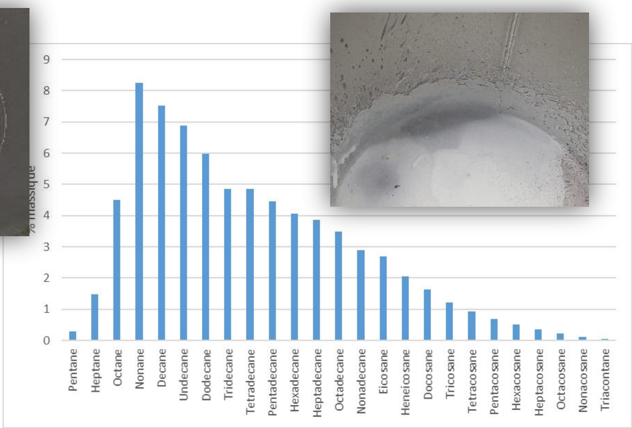
Labscale reactor
(0,8 Nm^3/h)
Selected catalyst

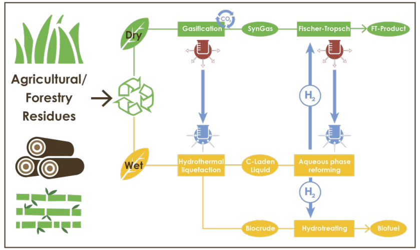
Tests

Support the demo scale reactor design

Define optimal operation conditions

Demo scale reactor
(1,5 Nm^3/h)
To be implemented in Vienna





Millistructured Heat Exchangers Reactors for Power to X applications: Overview of the demos

KHIMOD ALCEN

CO2-SNG (Poland)
KIC InnoEnnergy
100kWe
5 Nm3/h CH_4

Méthycentre
French consortium
Methanisation &
syngas methanation
250kWe

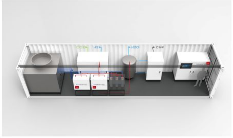
MÉTHYCENTRE

STORE&GO

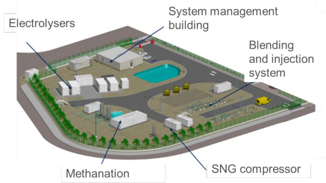
Supported by the State Secretariat for Education, Research and Innovation under contract no. 15.0333

Methanation CO_2,
200 kWe □ LNG

cea liten KHIMOD ALCEN



Jupiter 1000
French consortium
Methanation CO_2,
500 kWe



Heat to Fuel,
gaseification & HTL then FT

Heat to Fuel

Thanks!