European PhD Hydrogen Conference
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# Using $H_2$ for $CO_2$ activation on the way towards synthetic fuels

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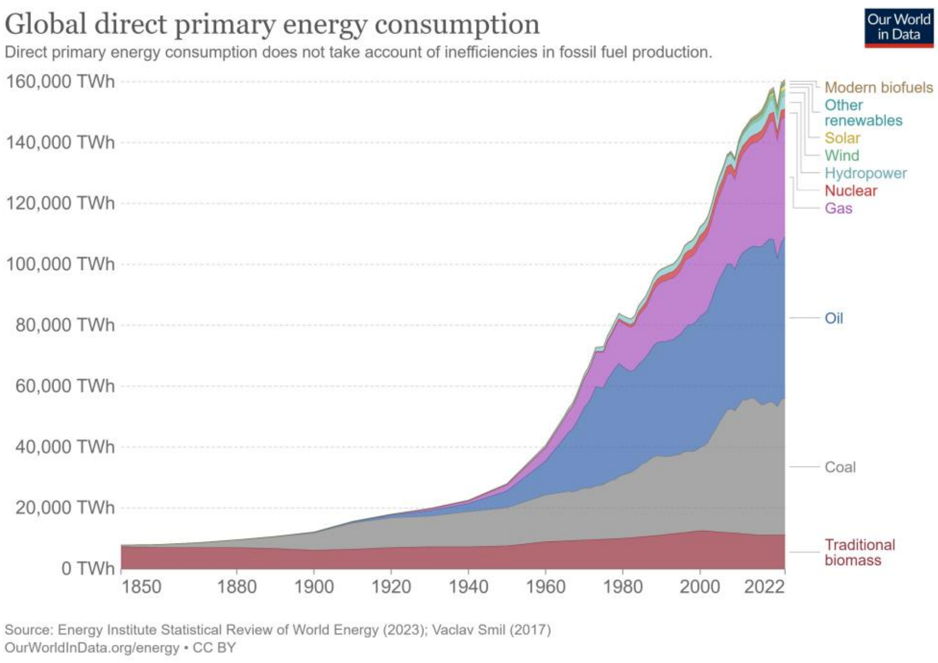
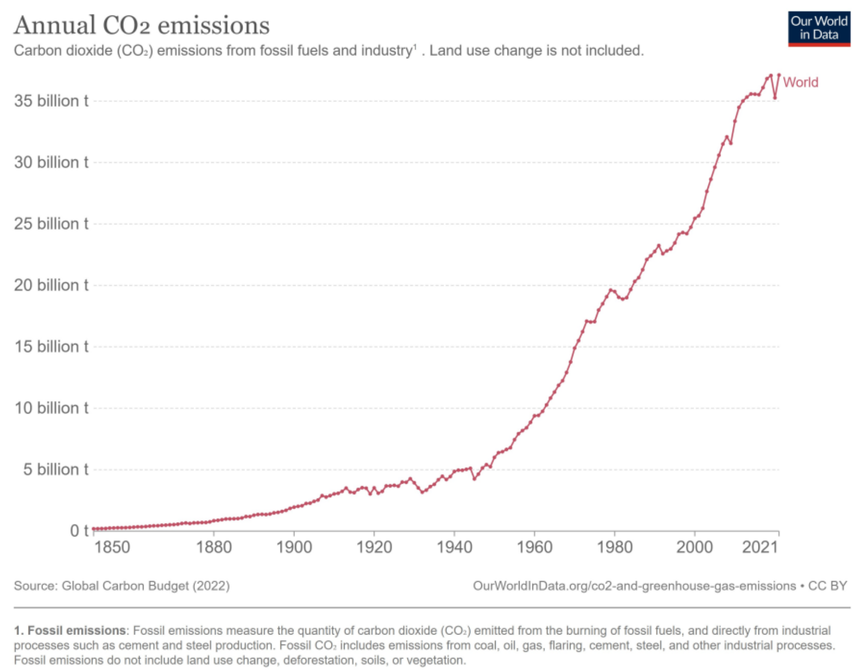
# The Energy Crisis: a dilemma

**Meet the increasing energy demand** >< **Limit GHG emissions**

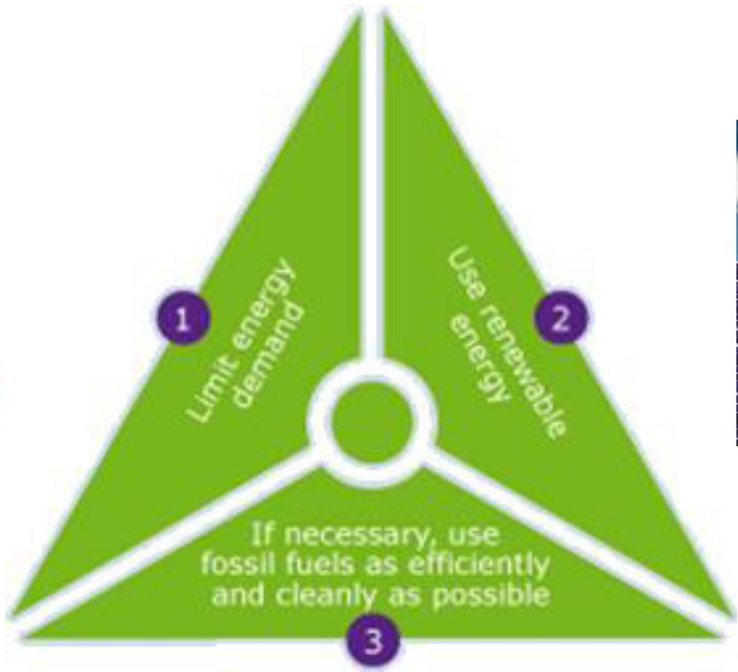



https://ourworldindata.org/grapher/global-primary-energy




*Hannah Ritchie, Max Roser and Pablo Rosado (2020) - "$CO_2$ and Greenhouse Gas Emissions". Published online at OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/co2-and-greenhouse-gas-emissions' [Online Resource]*

# A possible solution: the Trias Energetica

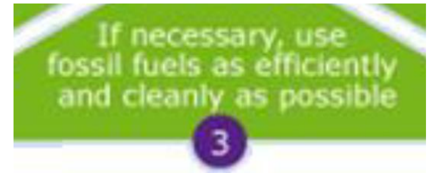




*Lysen, E H. The Trias Energica: Solar energy strategies for developing countries. Germany: N. p., 1996. Web.*

# Implications of the Trias Energetica concept

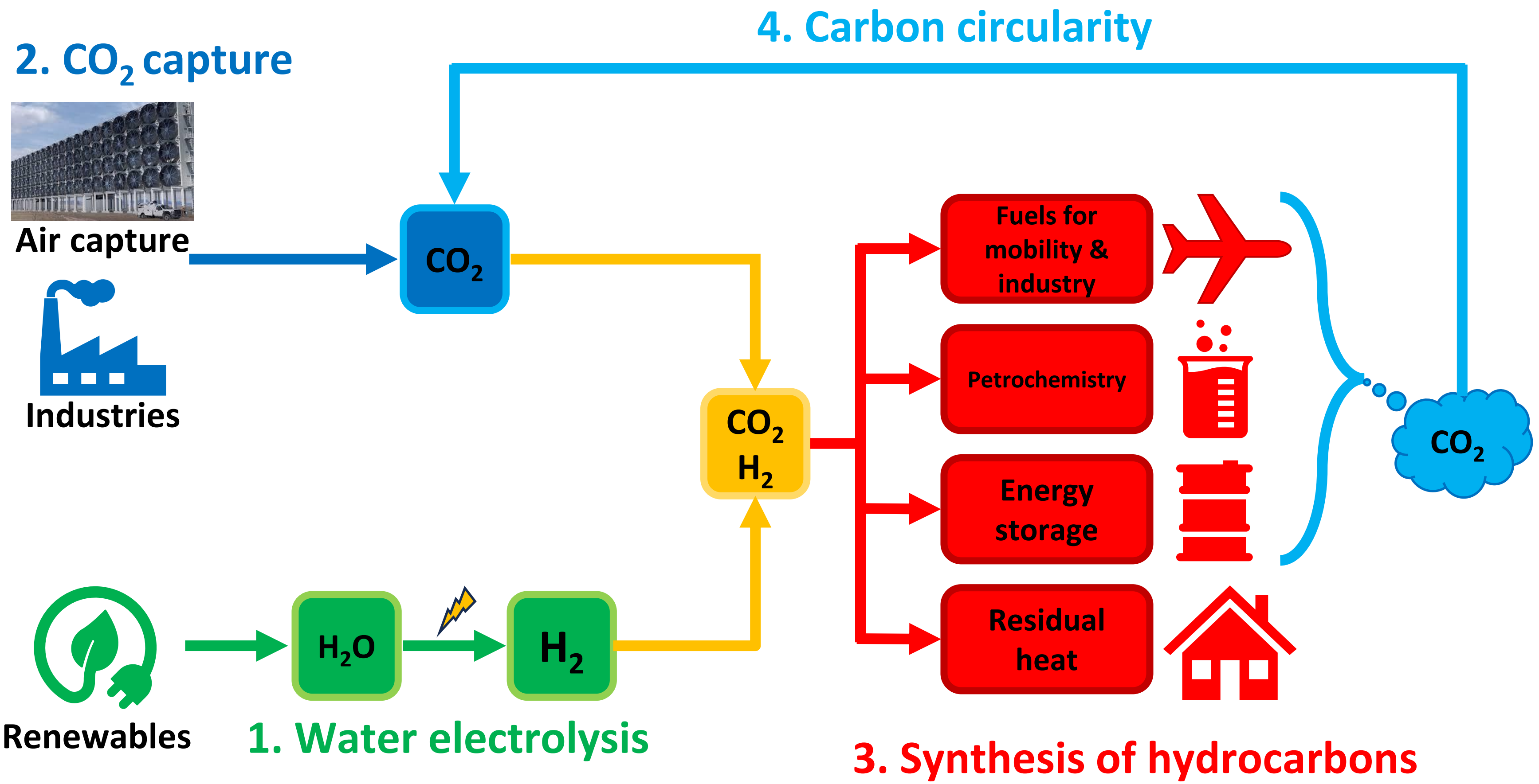

- Variable (time)
  - **storage** required
- Variable (location)
  - **transport** required



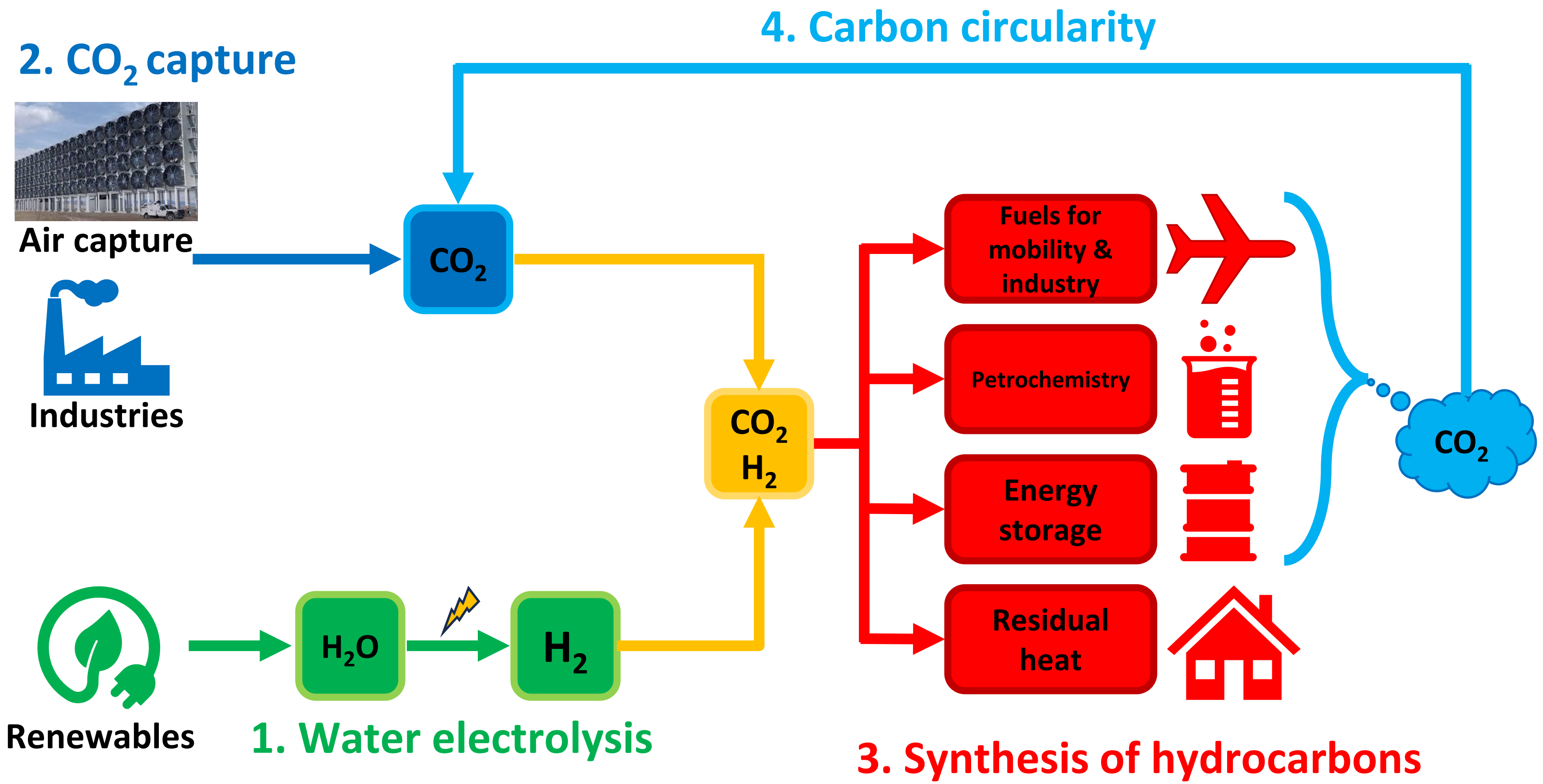


- Large amount of **$CO_2$ available**

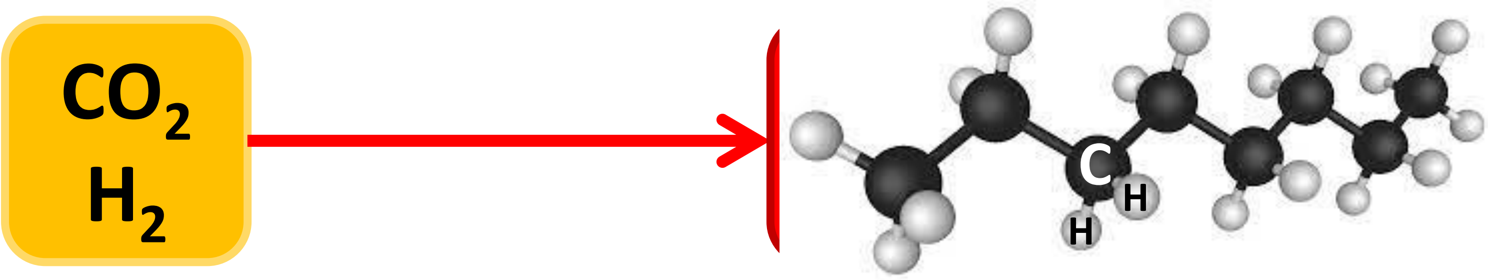
# The power-to-fuel concept



# The power-to-fuel concept



# From the $CO_2$ molecule to the synthetic fuel…




$$n\,CO_2 + (3n+1)\,H_2 \leftrightarrow C_nH_{2n+2} + 2n\,H_2O$$

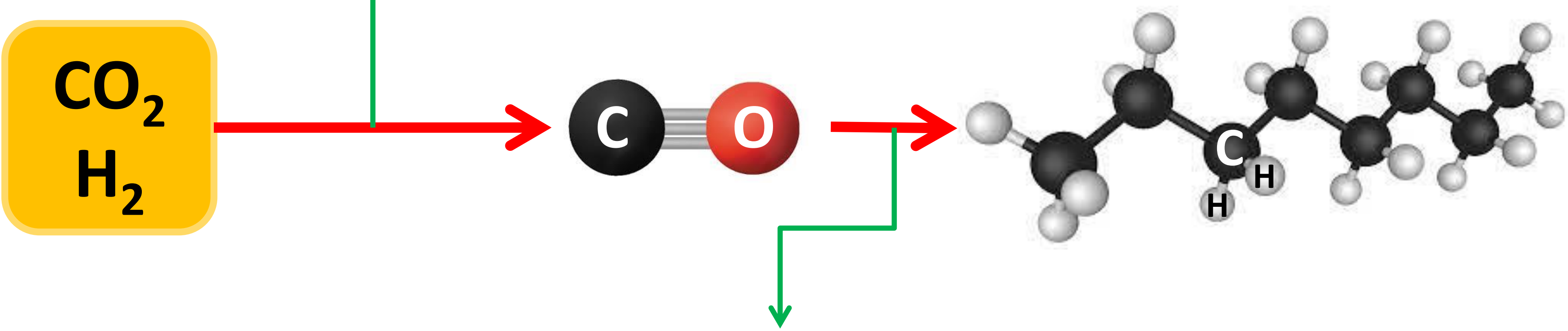
- Reaction difficult to achieve in a single step
  - $CO_2$ molecule highly stable
  - C-C bonds hard to form

**Indirect synthesis of synthetic fuels**

# From the $CO_2$ molecule to the synthetic fuel…

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

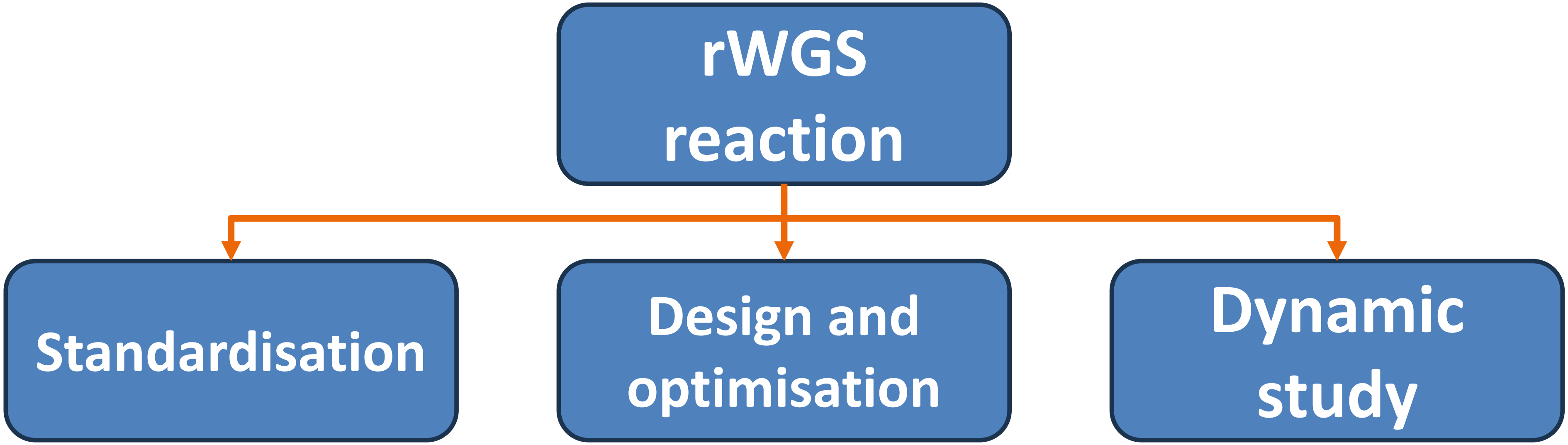
reverse water-gas shift reaction (rWGS)

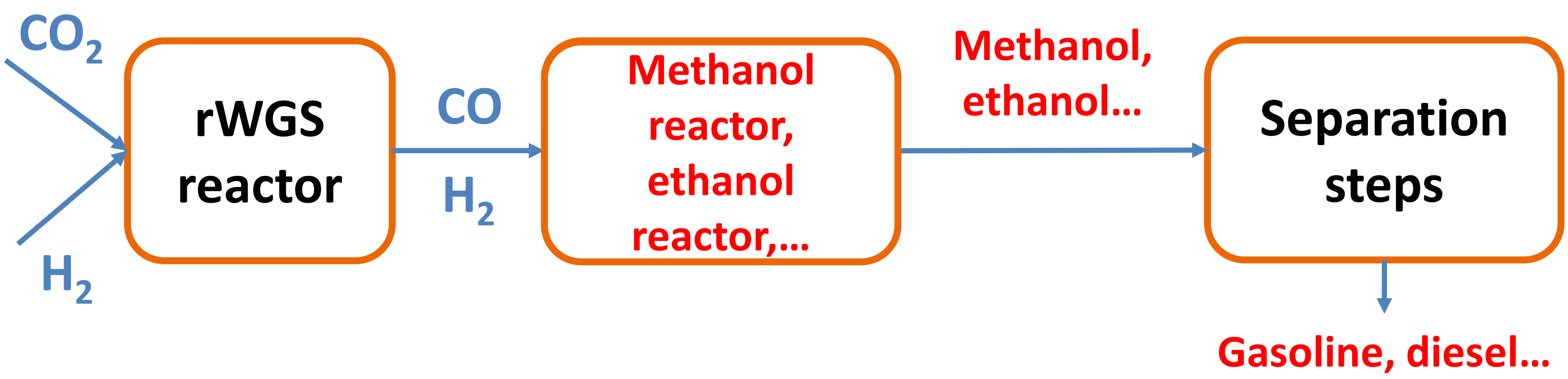



$$n\,CO + (2n+1)\,H_2 \leftrightarrow C_nH_{2n+2} + n\,H_2O$$

Fischer-Tropsch reaction

# Objectives of our work



# rWGS reaction operating conditions

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad \Delta H° = +41\ kJ/mol$$

$$CO_2 + 4\ H_2 \Leftrightarrow CH_4 + 2\ H_2O \qquad \Delta H° = -165\ kJ/mol$$

$$CO + 3\ H_2 \Leftrightarrow CH_4 + H_2O \qquad \Delta H° = -206\ kJ/mol$$

+ exothermic **solid carbon** formation

*Table 1 - Operating conditions applied for the rWGS reaction in different simulation works*

| Reference | Temperature (°C) | Pressure (bar) |
|---|---|---|
| Adelung, Maier, and Dietrich (2021) | 550 – 950 | 1 – 25 |
| Bown et al. (2021) | 665 – 750 | 1 |
| Elsernagawy et al. (2020) | 350 – 940 | 1 – 30 |
| Ghodoosi, Khosravi-Nikou, and Shariati (2017) | 400 – 700 | 1 |
| Kaiser et al. (2013) | 1000 | 30 |
| König et al. (2015) | 900 | 25 |
| Comidy, Staples, and Barrett (2019) | 950 | 25 – 30 |
| Rezaei and Dzuryk (2019) | 900 | 4.2 |
| Unde (2012) | 1000 – 1200 | 1 – 30 |
| Vázquez et al. (2018) | 980 – 1000 | 20 |
| Wenzel, Rihko-Struckmann, and Sundmacher (2017) | 800 | 1 |
| Wolf, Jess, and Kern (2016) | 900 | 30 |

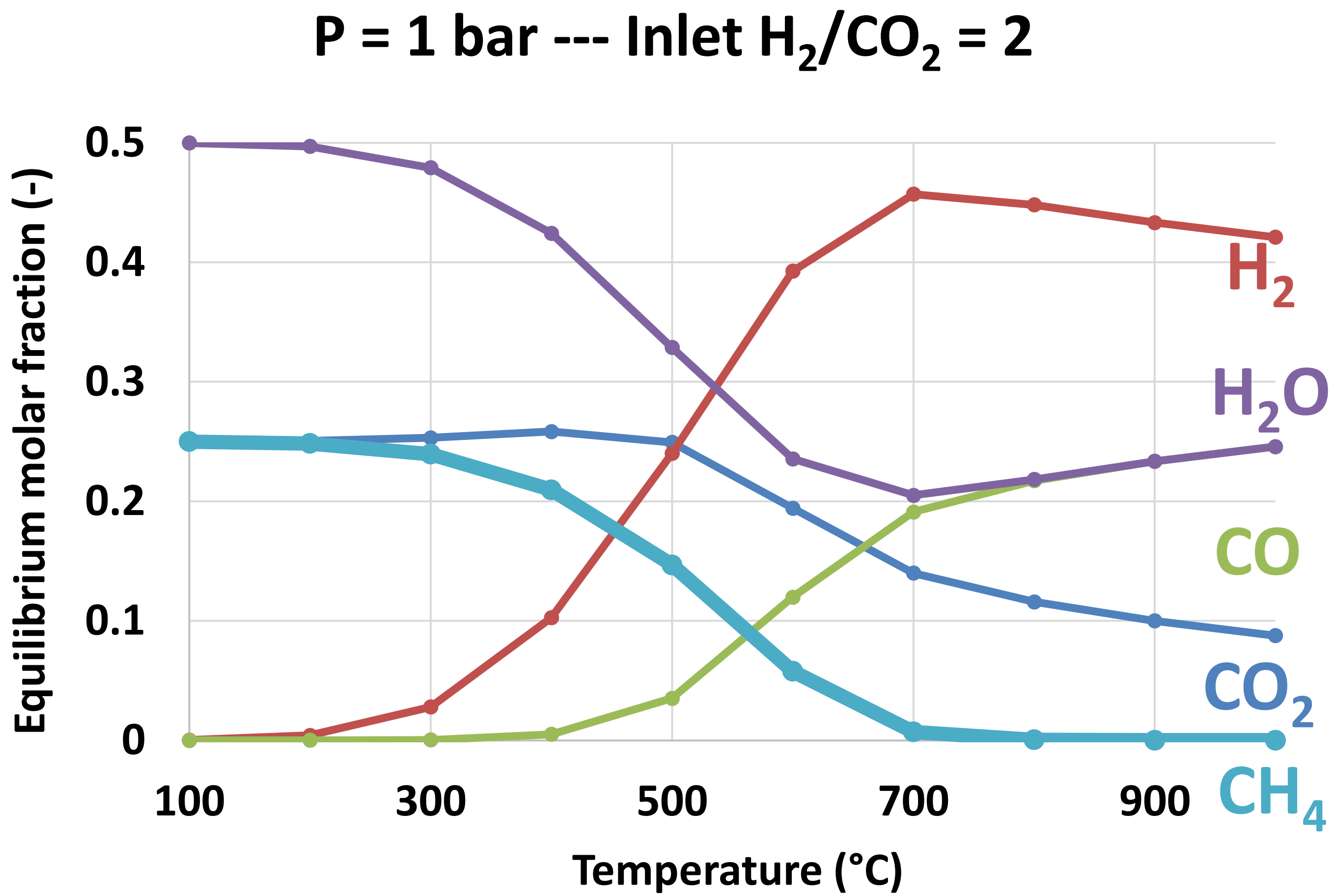
**T° ≈ 800 – 900°C**

**P ≈ 1 – 30 bar**



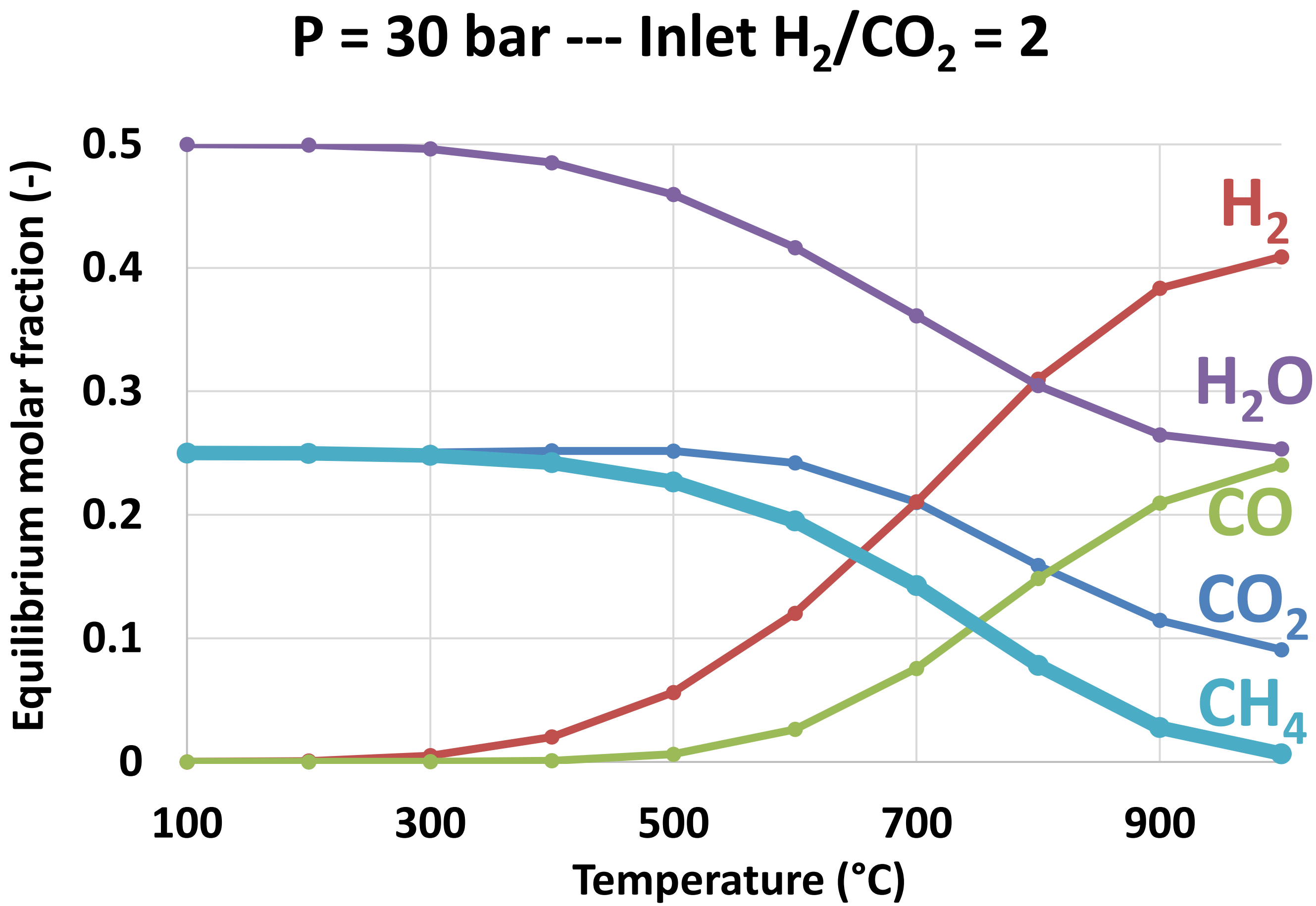
*A. Rouxhet, M. E. A. Berchiche, and G. Léonard, "A Review of the Reverse Water-Gas Shift Reaction as an Intermediate Step in Power-to-Fuels Processes." unpublished.*

# rWGS reactor at equilibrium – conditions influence



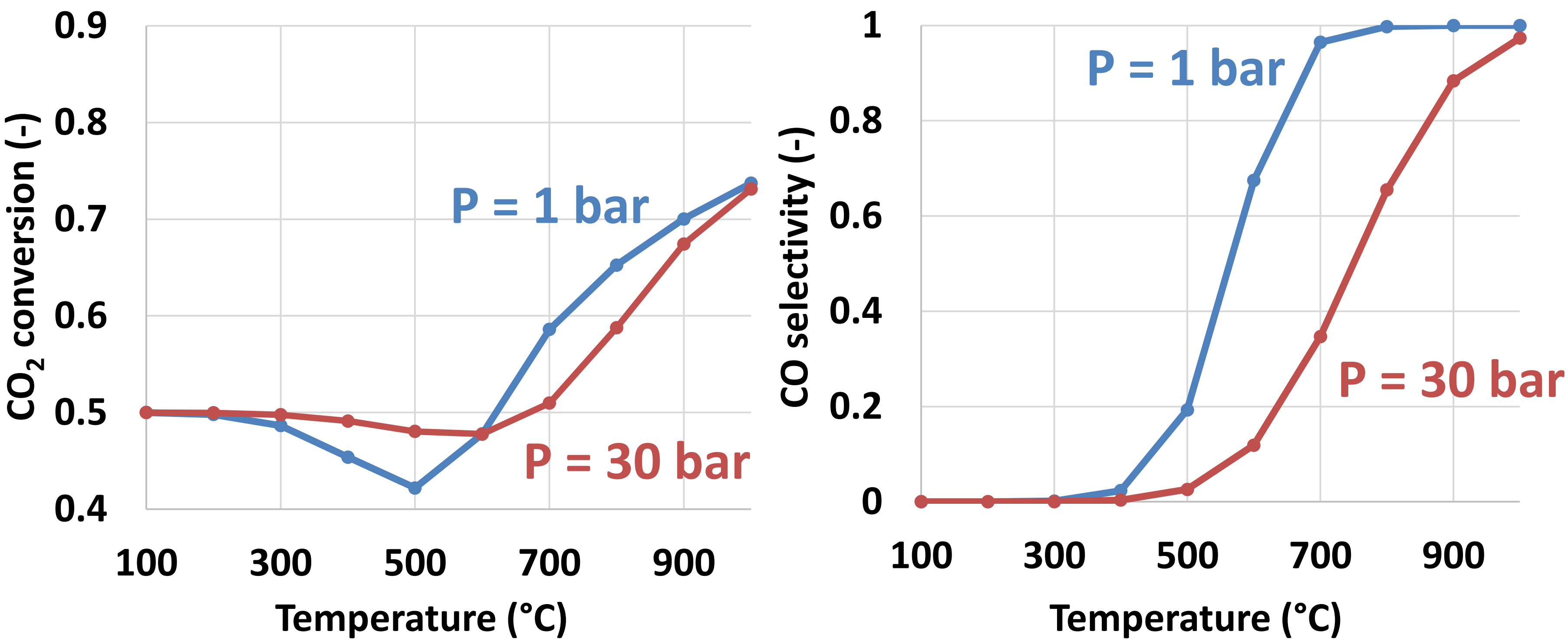

**$CH_4$ production limited above 700°C at 1 bar**

# rWGS reactor at equilibrium – conditions influence



# rWGS reactor at equilibrium – conditions influence

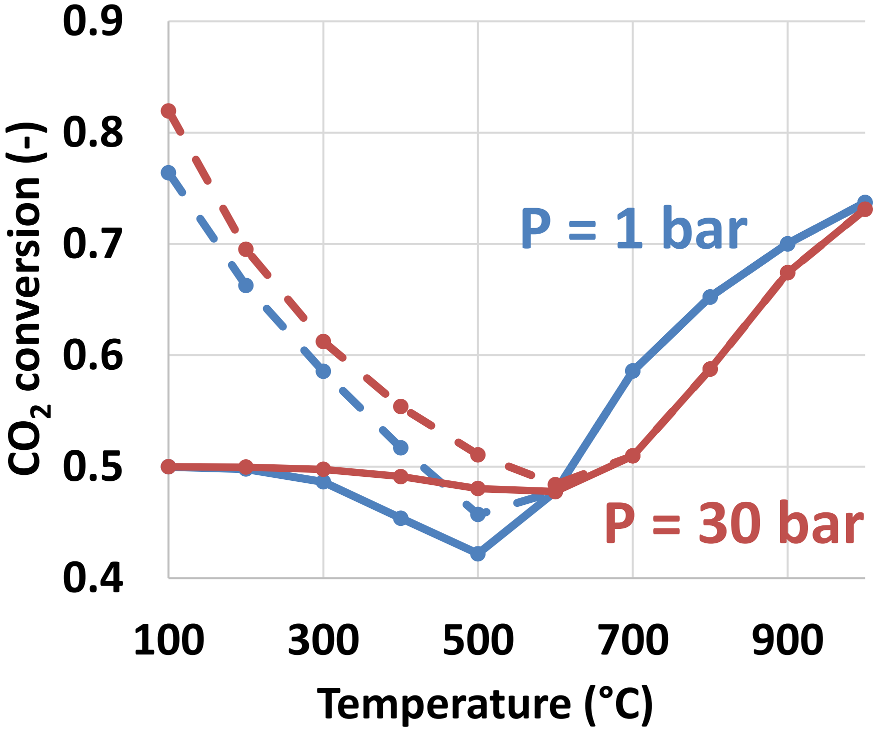
## Constant inlet $H_2/CO_2$ = 2

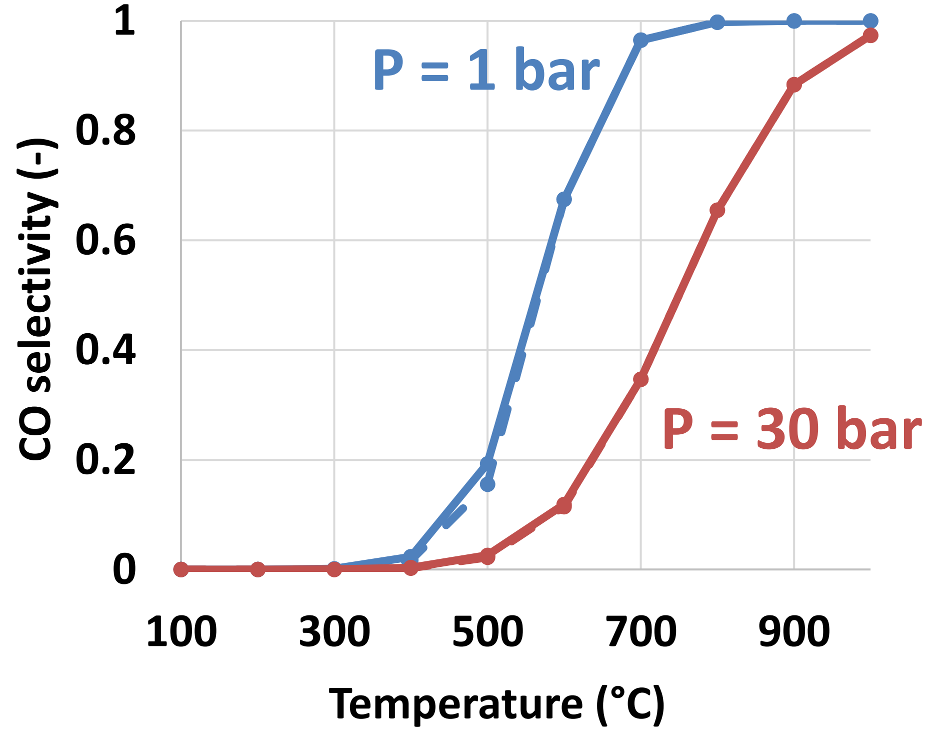



**$CO_2$ conversion and CO selectivity favoured at low pressure**

# rWGS reactor at equilibrium – conditions influence

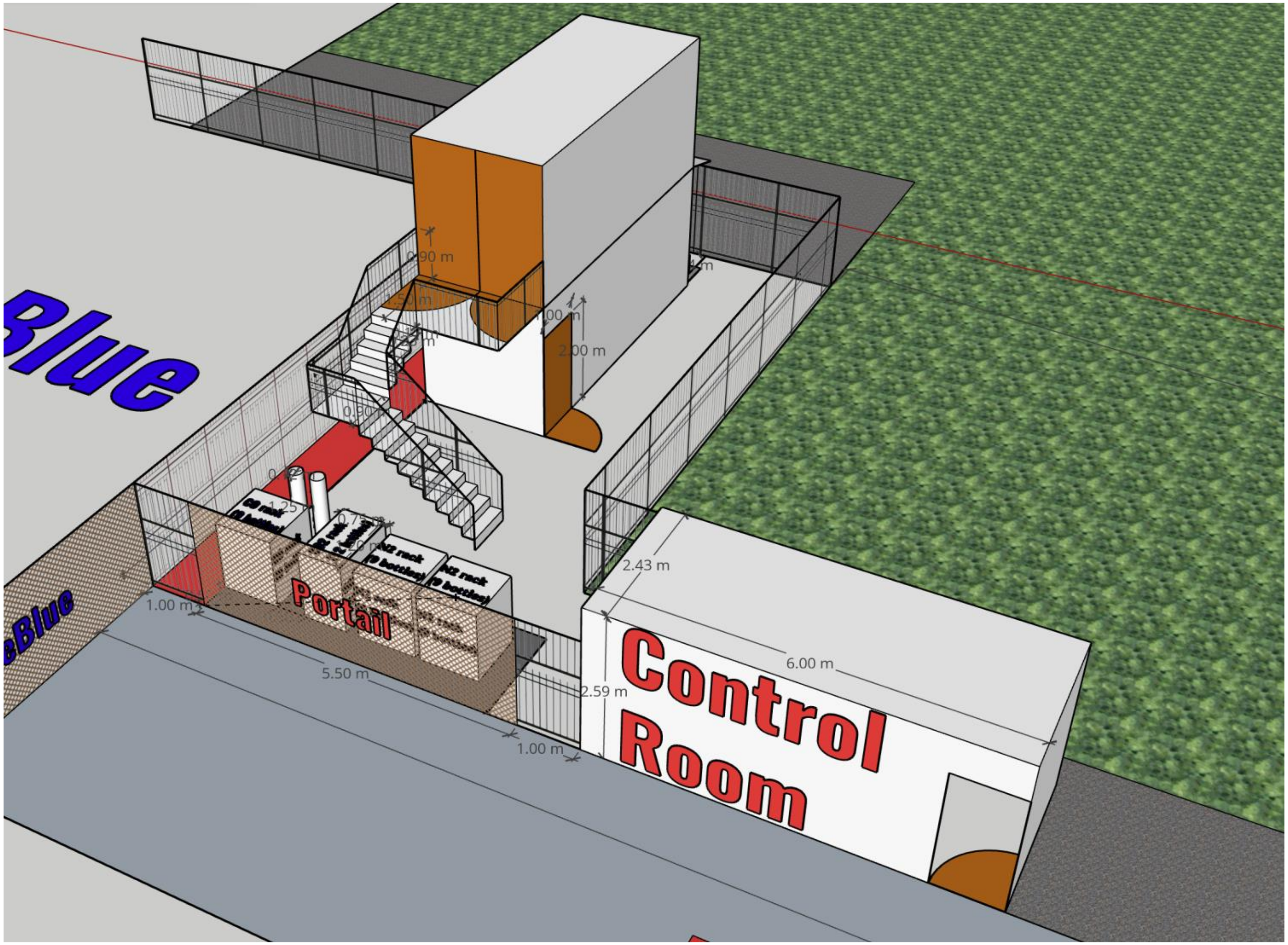
## Constant inlet $H_2/CO_2$ = 2



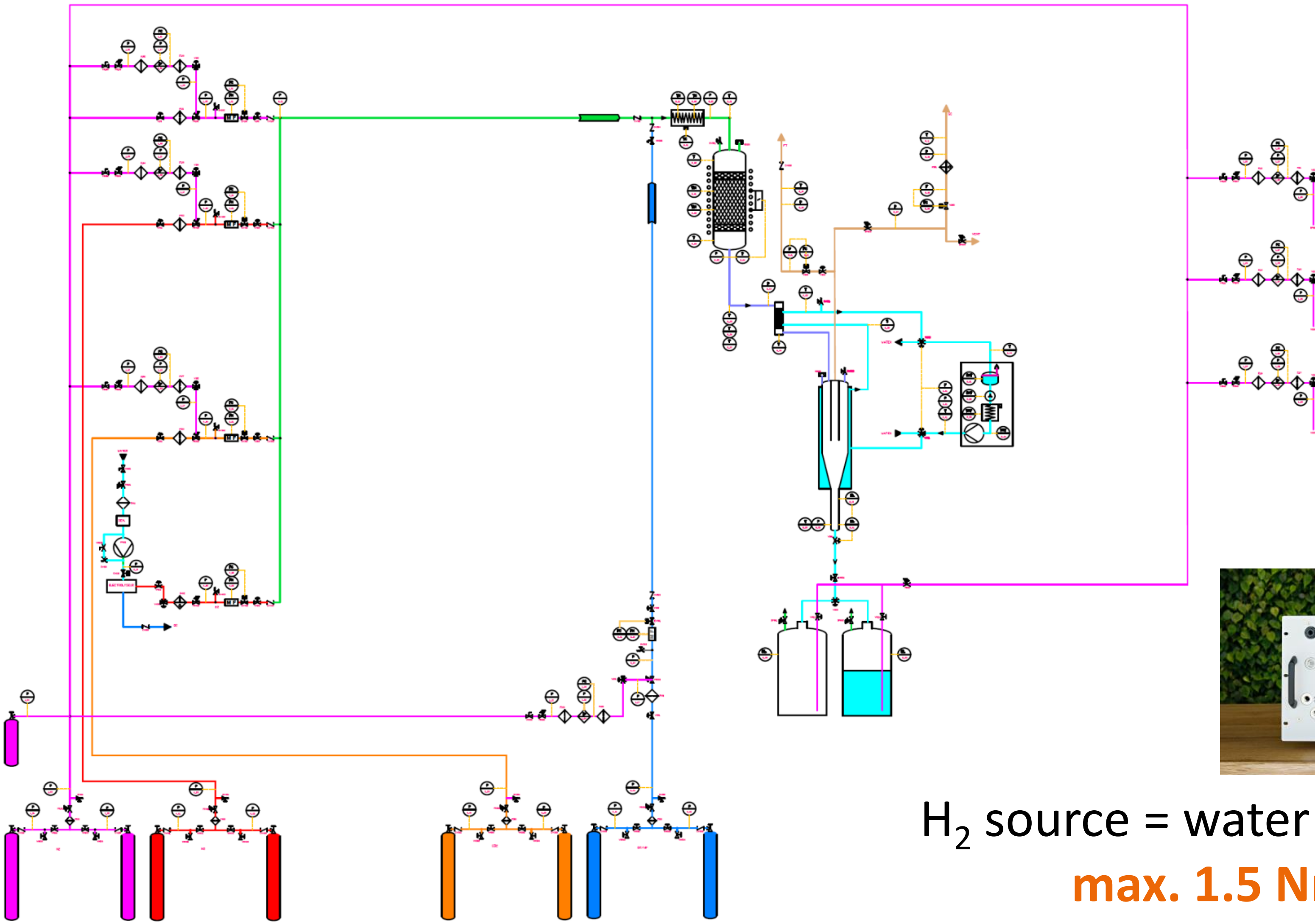




**Coking reaction only impacts $CO_2$ conversion at low temperature**

# Major perspective: a pilot-scale installation



# Major perspective: a pilot-scale installation

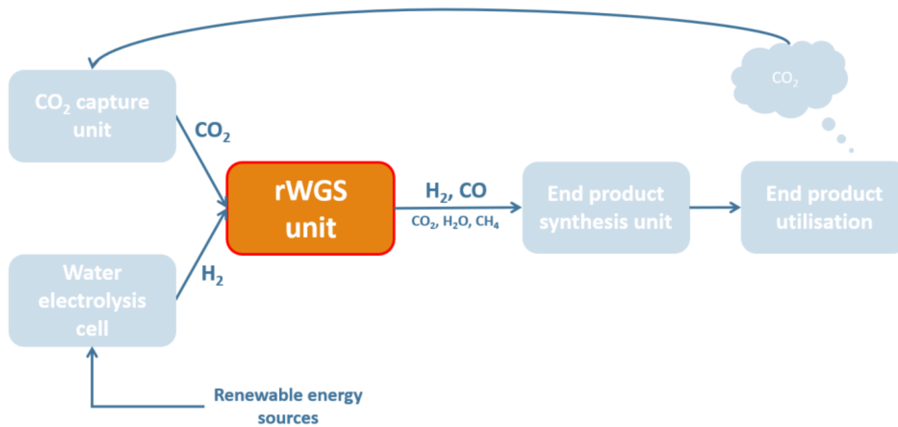



$H_2$ source = water electrolysis

**max. 1.5 Nm³/h**

# Take-home messages

- In the future, increasing need to store and transport energy
  - Power-to-fuel concept offers a solution
  - Fuels present high energy density per unit volume
- Indirect synthesis from captured $CO_2$ and $H_2$
  - rWGS pathway = $CO_2$ activation by transformation into CO
- High temperature required to limit $CH_4$ production
- Optimal pressure not as straightforward
- **Pilot installation converting $CO_2$ to kerosene soon at ULiège**




# Thank you for your attention!

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