Co-production of Diesel and Synthetic Natural Gas from the Olive Oil Industry Waste

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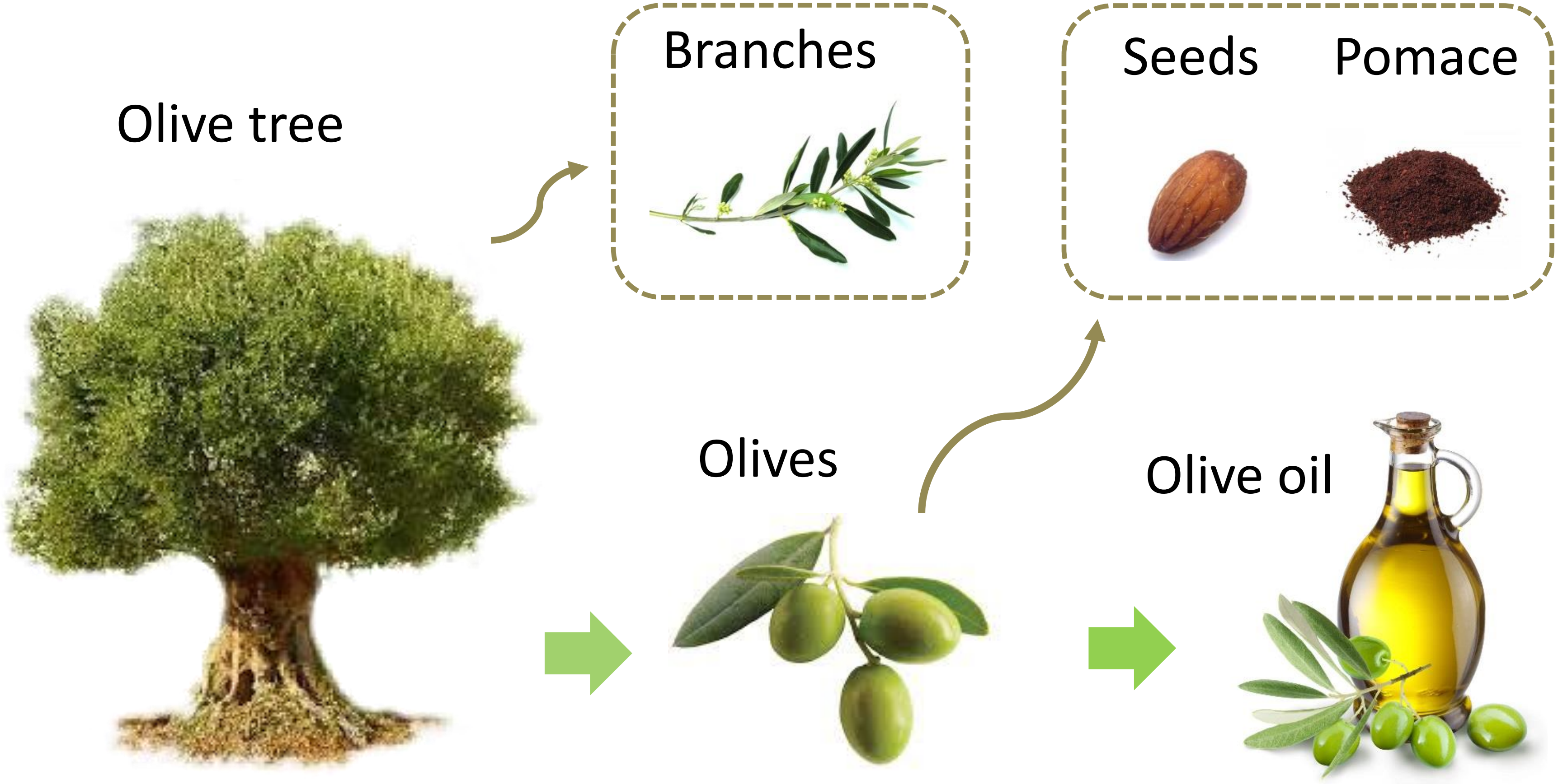
KTH – Chemical Technology

Outline

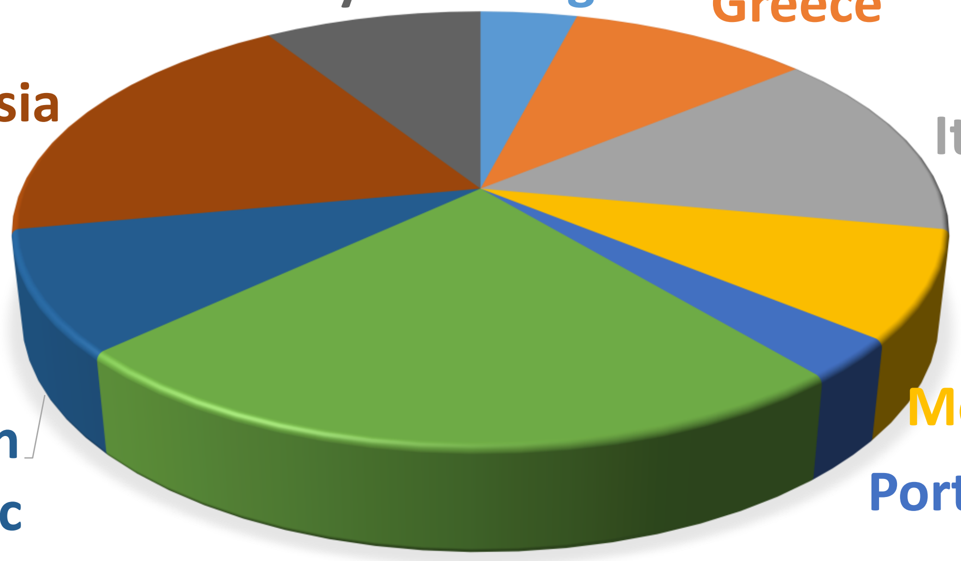
1. Setting the scene
2. The fuel production process
3. The Fischer-Tropsch synthesis - Diesel production
4. Methanation – Synthetic natural gas (SNG) production

1. Setting the scene



1. Setting the scene

Olive production uses a significant part of the available land in Mediterranean countries



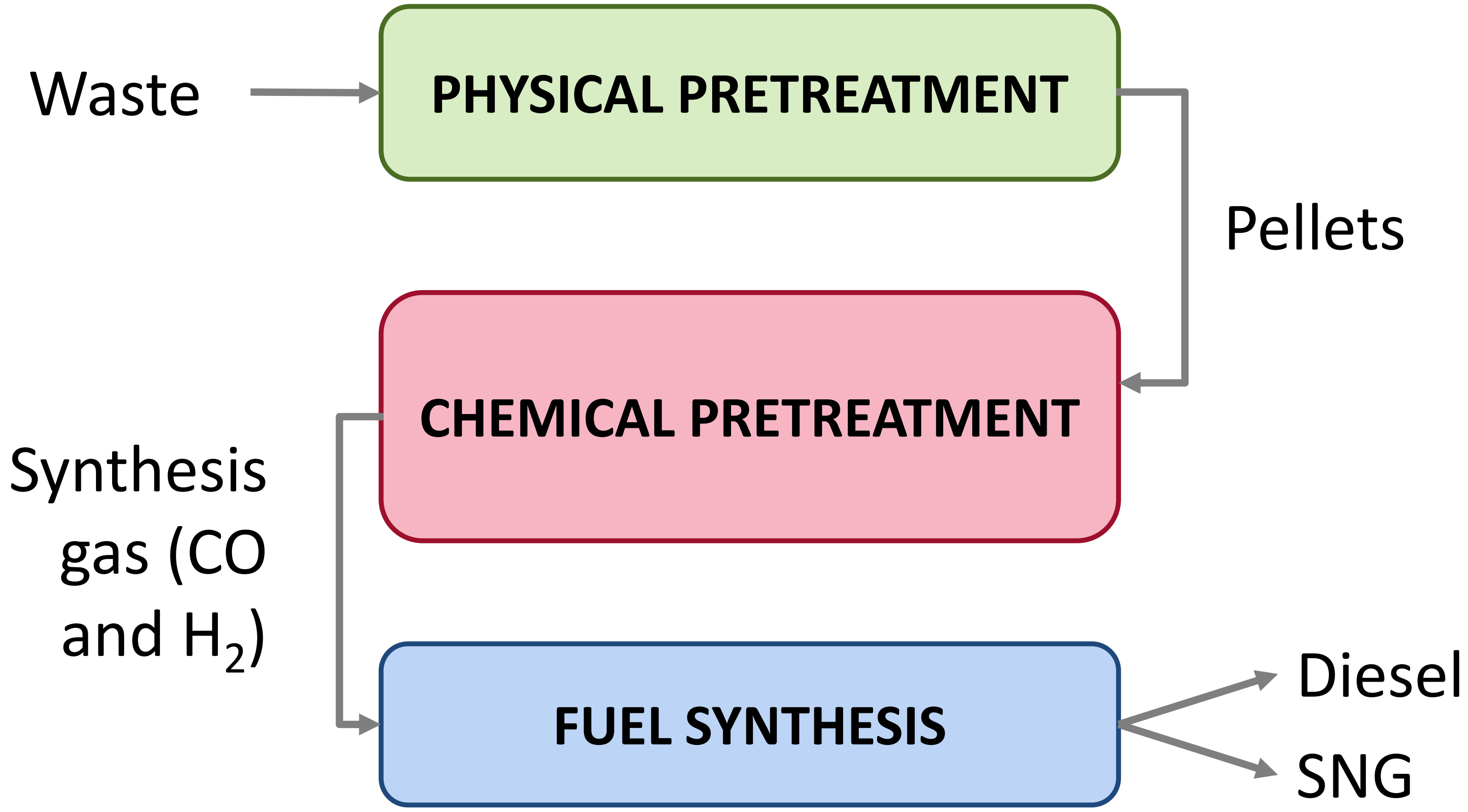
Harvested area 2010 > 8 000 000 Ha → Residues > 14 Mt!

Ref: European Commission. Environment. Life among the olives. Good practice in improving environmental performance in the olive oil sector. [Online] 26-01-2010

1. Setting the scene

- Alternative to fossil fuels
- Reduction of greenhouse gas emissions

2. The fuel production process



2. The fuel production process

PHYSICAL PRETREATMENT

Waste

Drying
Grinding
Mixing
Pelletizing

Pellets

2. The fuel production process

CHEMICAL PRETREATMENT

Pellets

Gasification

Tar removal

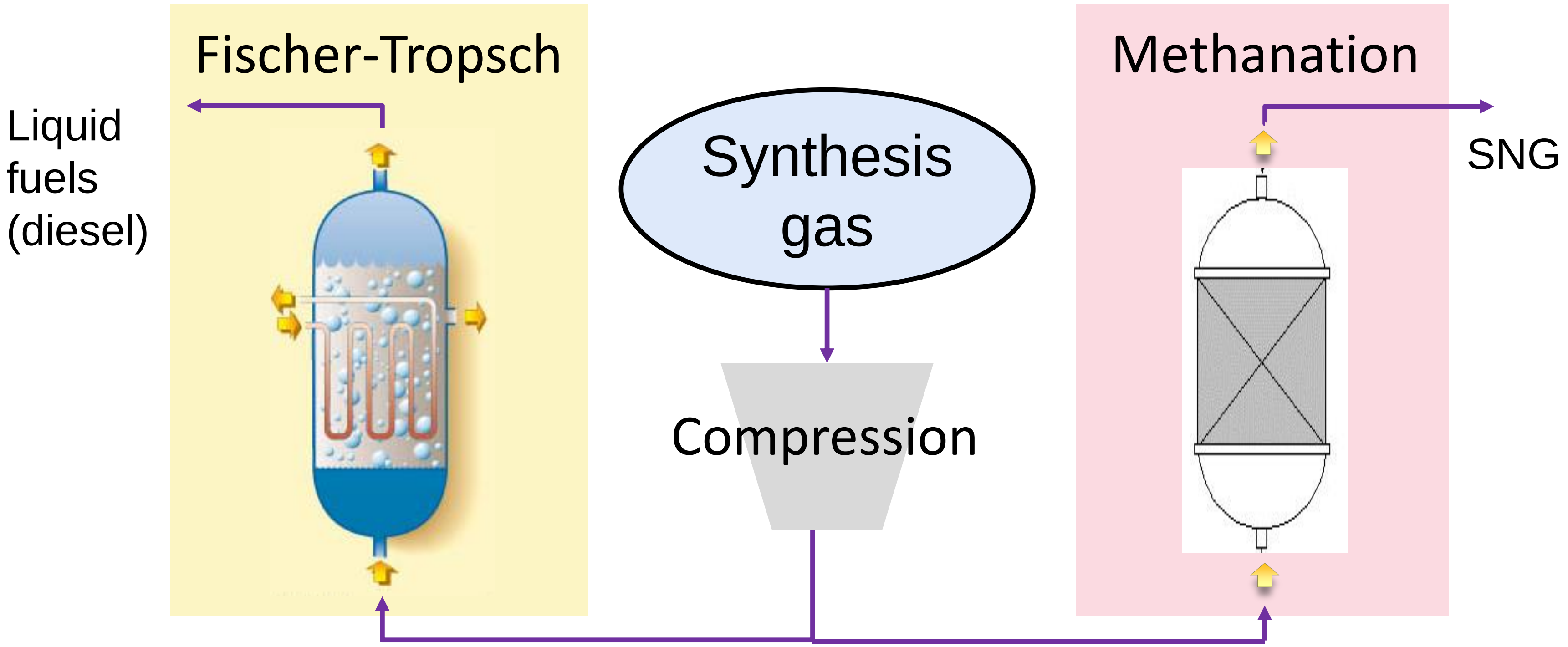
CO_2 removal

Purification (e.g. H_2S removal)

Synthesis gas

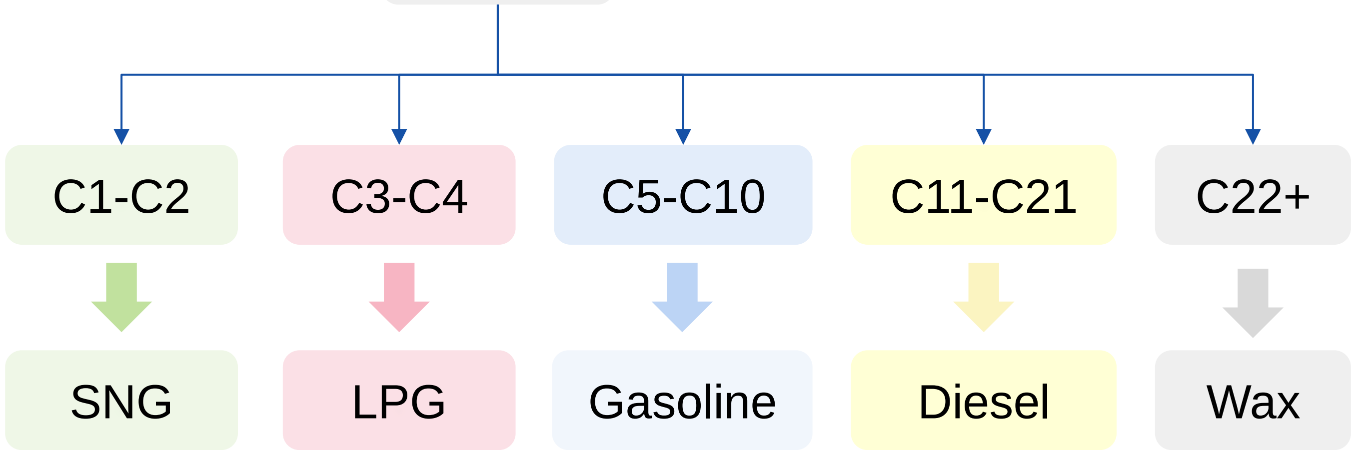
2. The fuel production process

FUEL SYNTHESIS



3. The Fischer-Tropsch Synthesis

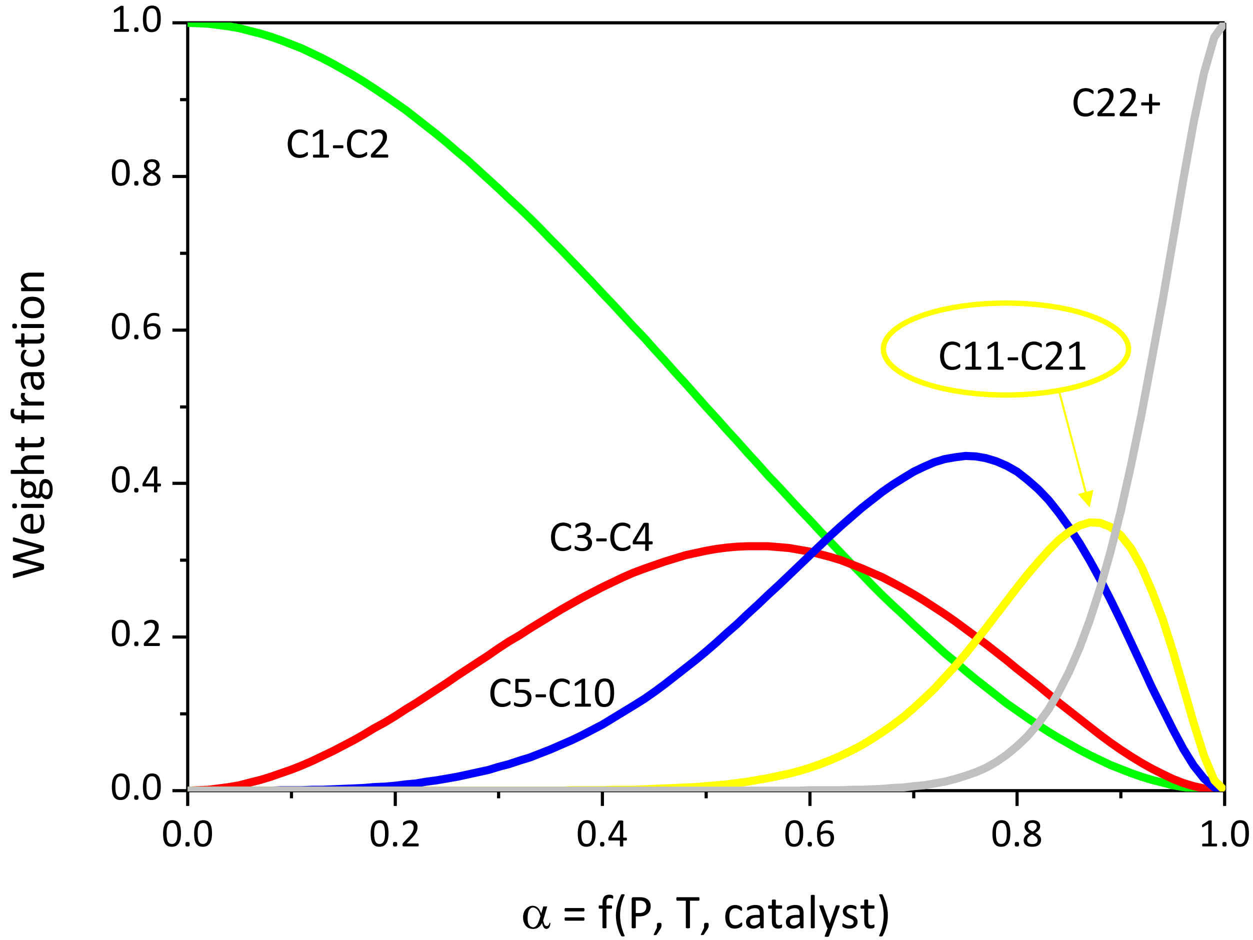
$$CO + 2H_2 \rightarrow -CH_2- + H_2O \qquad (\Delta\hat{H}^\circ = -165\ kJ/mol)$$



$$Temperature \uparrow \;\Rightarrow\; Selectivity\ to\ long\ chain\ hydrocarbons \downarrow$$

$$Pressure \uparrow \;\Rightarrow\; Selectivity\ to\ long\ chain\ hydrocarbons \uparrow$$

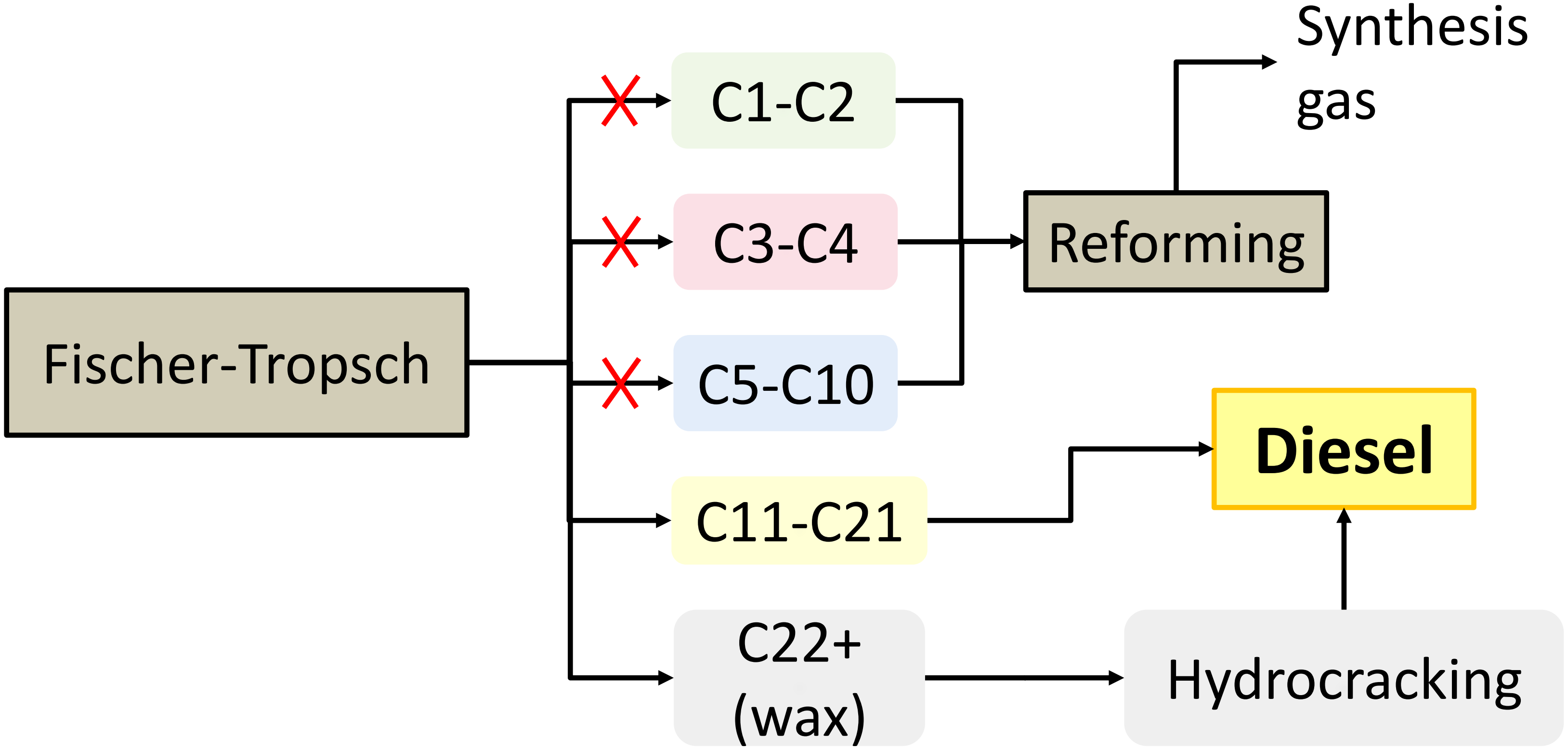
3. The Fischer-Tropsch Synthesis



It is impossible to only produce hydrocarbons in the carbon number range of C11-C21!

3. The Fischer-Tropsch Synthesis

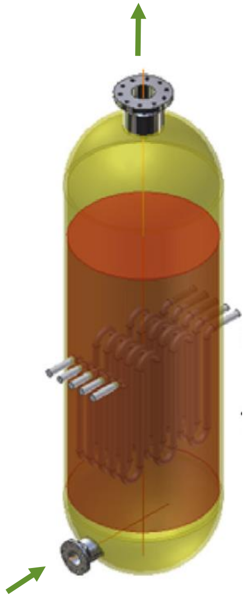
Diesel production optimization



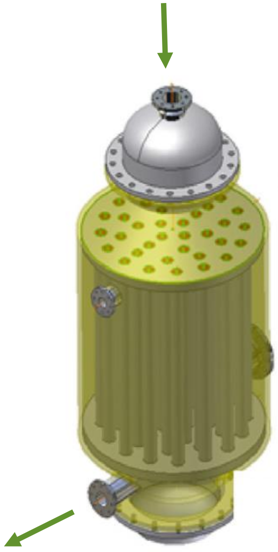
Diesel is maximized by optimizing the selectivity to C22+

3. The Fischer-Tropsch Synthesis

Slurry bed reactor



Multitubular fixed bed reactor



Reactor optimization

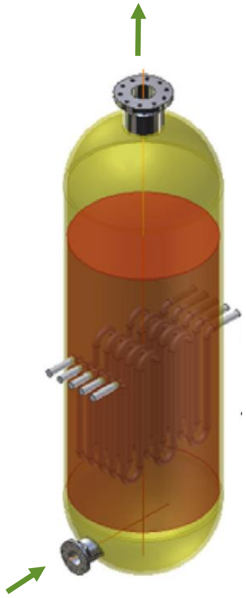
T = 200-250 °C
P = 20-40 bar

Hot spots ➡ *Selectivity to long chain hydrocarbons* ↓↓↓

Goal: Isothermal operation

3. The Fischer-Tropsch Synthesis

Slurry bed reactor



Catalyst optimization

- High activity, selectivity and **stability**
- High attrition resistance

Catalyst particle size: 50-100 µm

3. The Fischer-Tropsch Synthesis

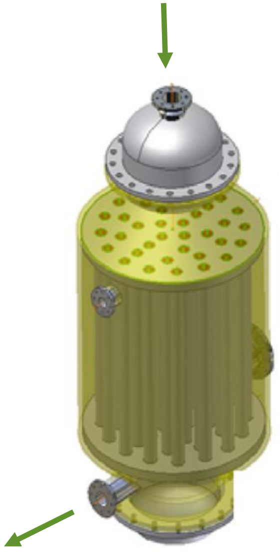
Catalyst optimization

- High activity, selectivity and **stability**
- Mass transfer

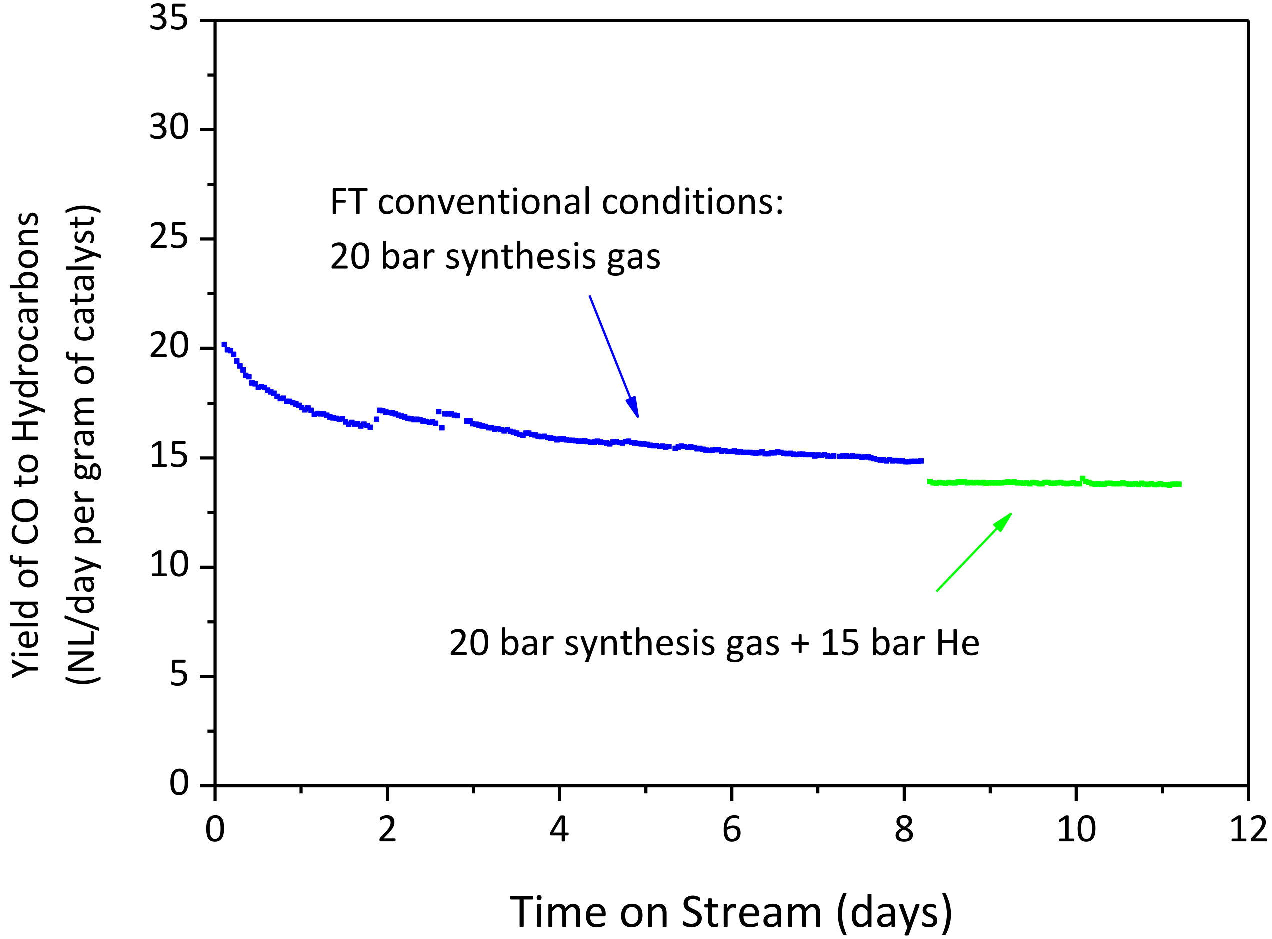
Catalyst particle size: > 1mm

Egg-shell catalyst:

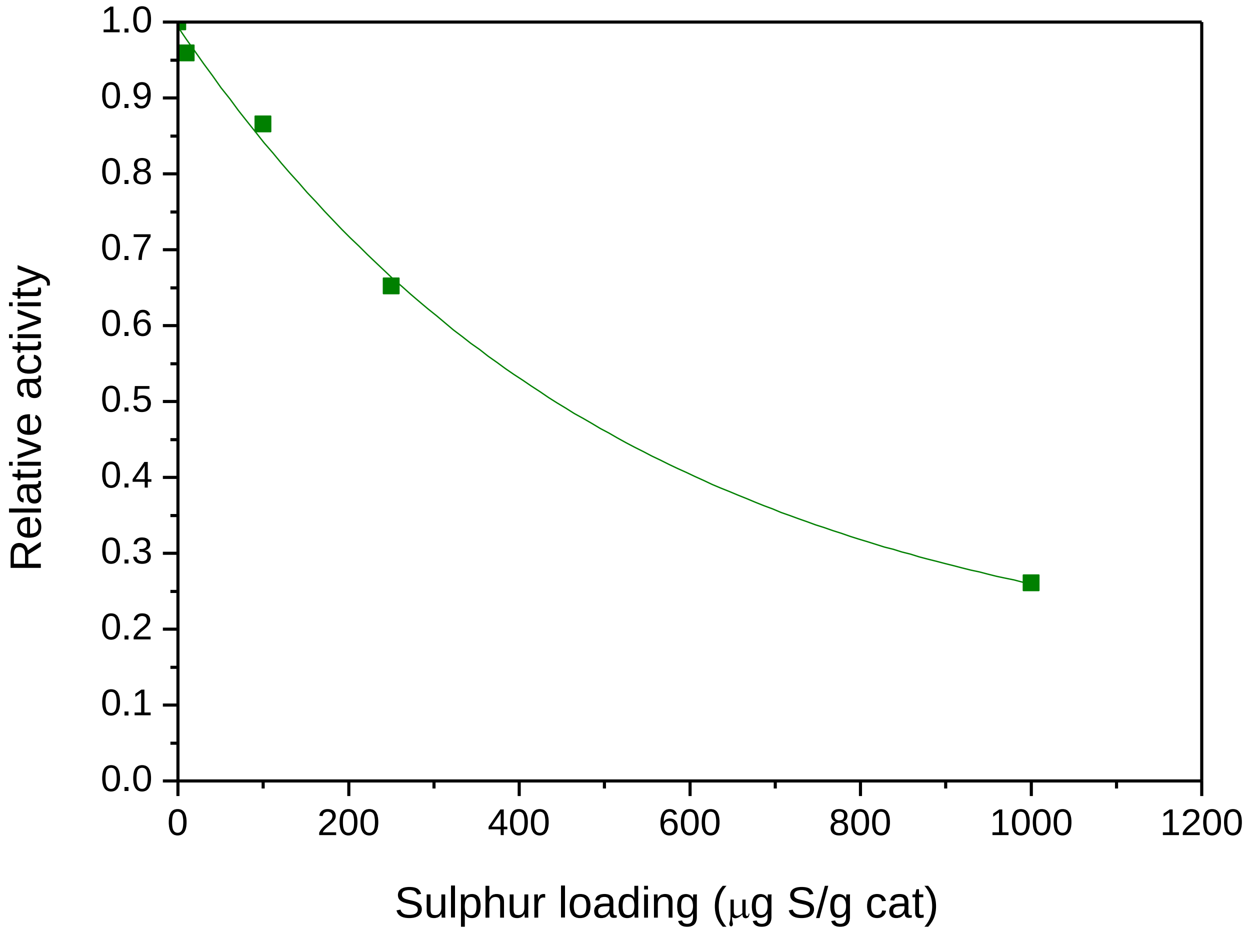
Multitubular fixed bed reactor



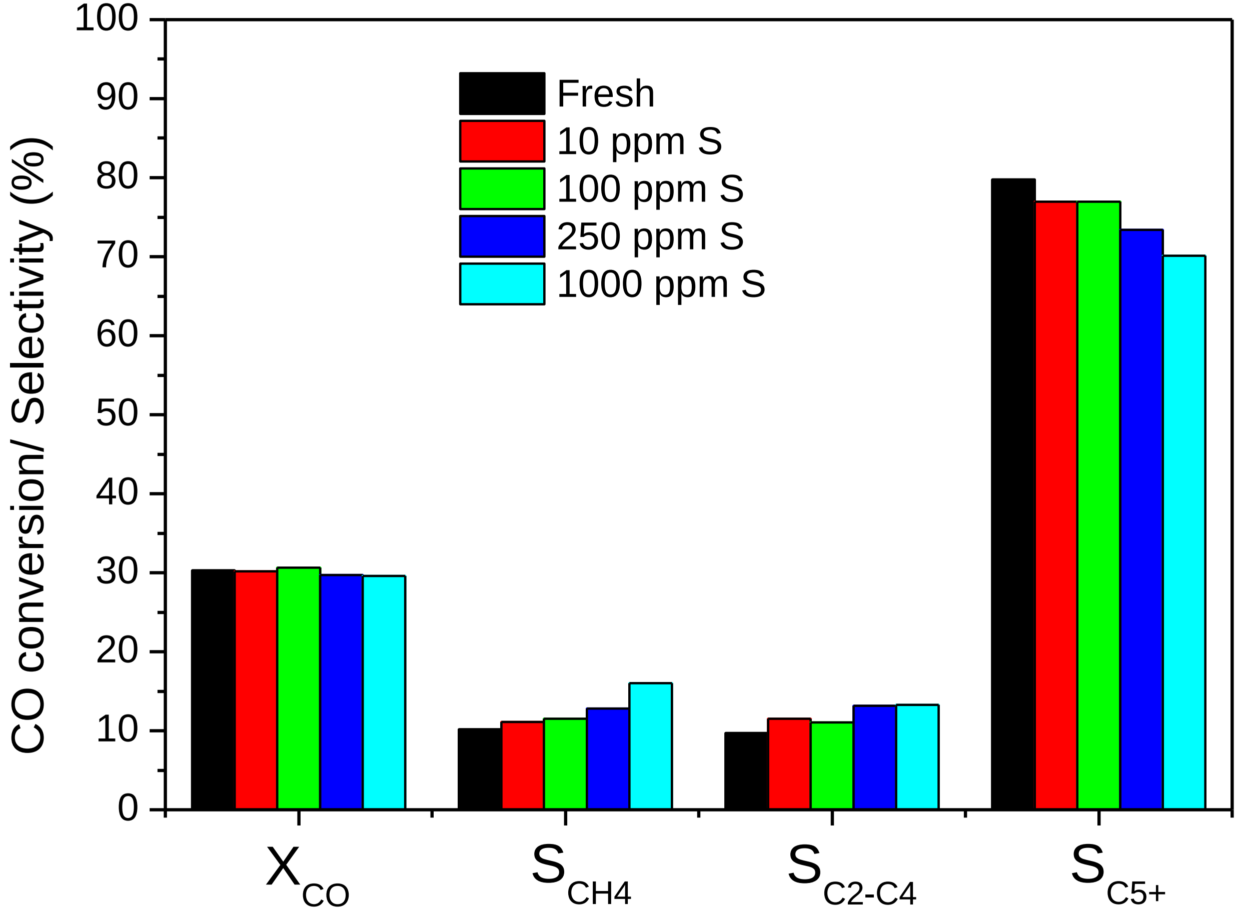
3. The Fischer-Tropsch Synthesis



3. The Fischer-Tropsch Synthesis



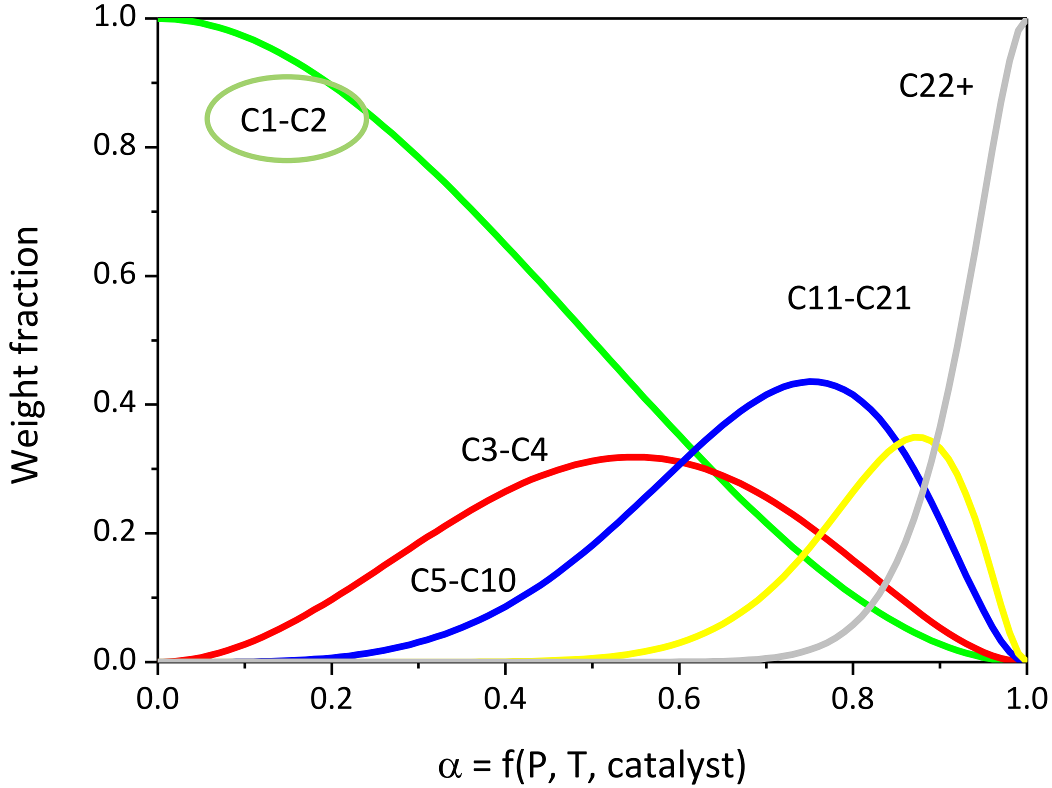
3. The Fischer-Tropsch Synthesis



Operating conditions: 20 bar, 210 °C and $H_2/CO=2.1$

4. Methanation

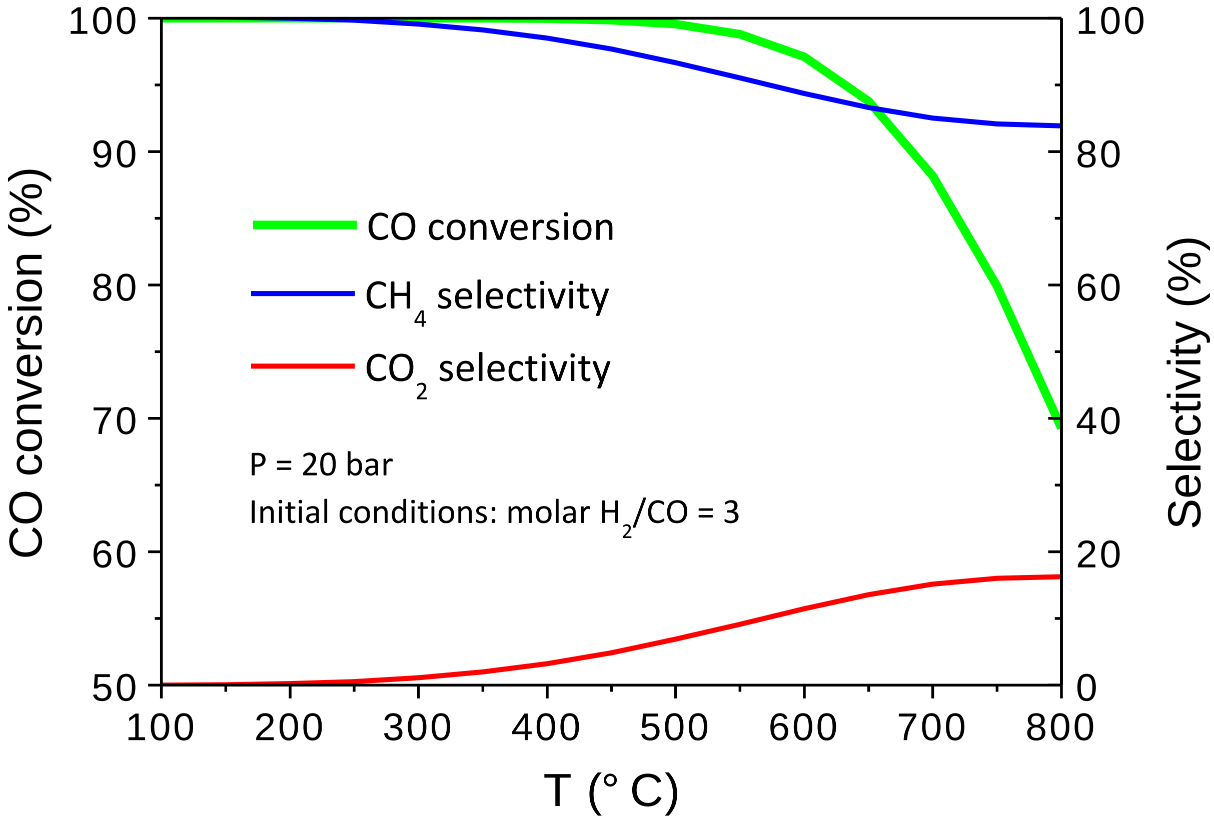
$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (\Delta\widehat{H}° = -206\ kJ/mol)$$



T ↑↑ ➡ Selectivity to CH_4 ↑↑↑

4. Methanation

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta\hat{H}^\circ = -41\ kJ/mol)$$

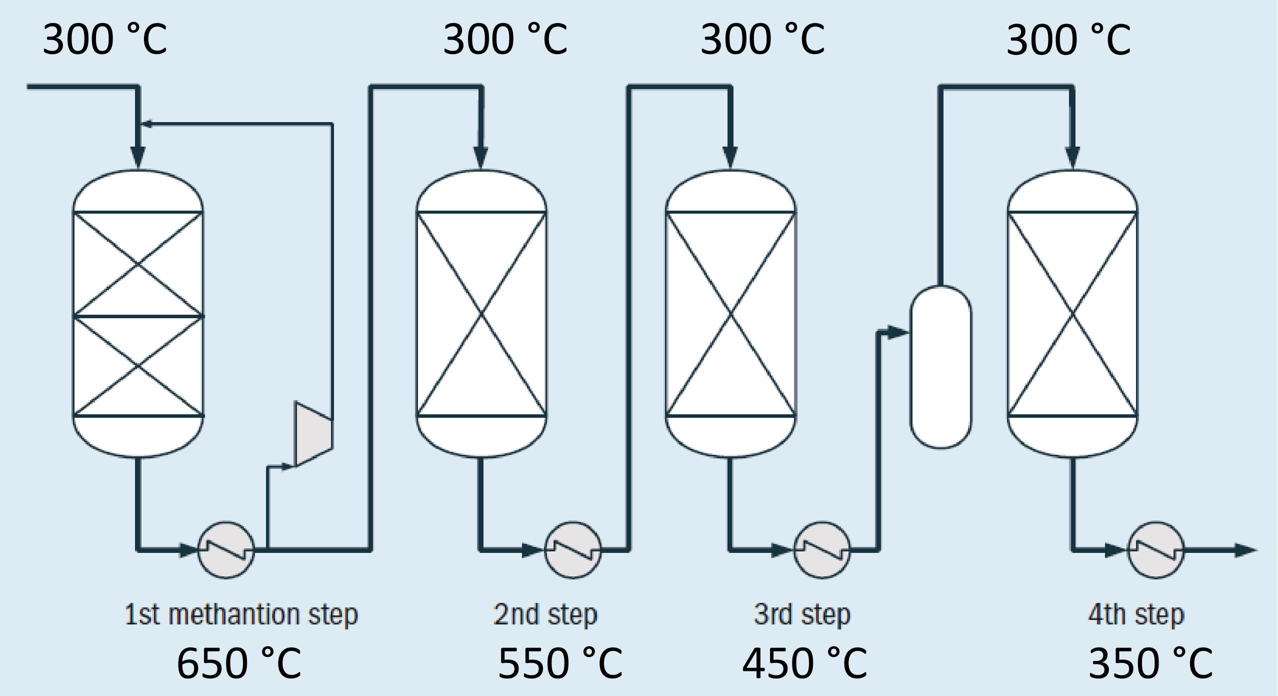


T ↑↑ ➡ Selectivity to CO_2 ↑↑↑

4. Methanation

Reactor/process optimization

T = 250-650 °C
P = 20-40 bar



4. Methanation

Catalyst optimization → Minimize catalyst deactivation!

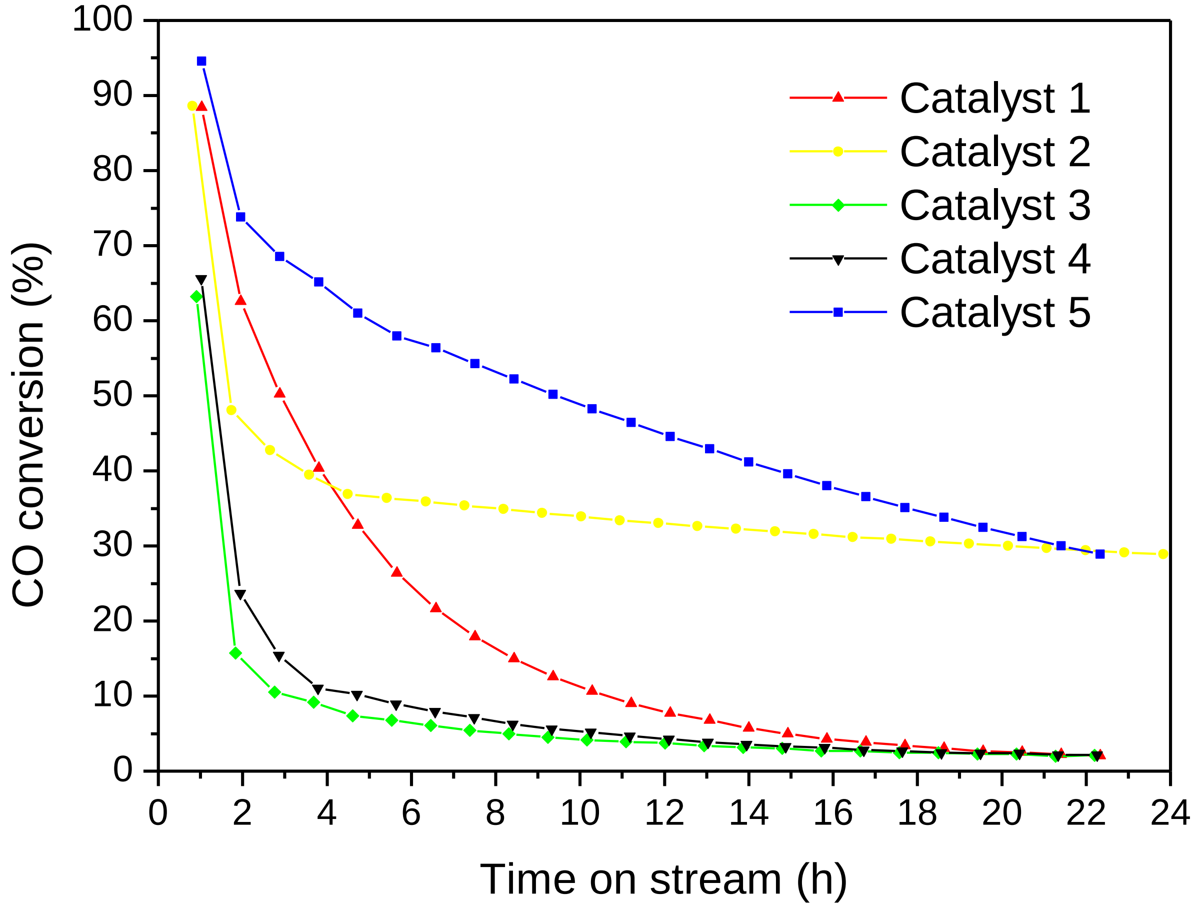
Preeminent methanation catalyst: **Nickel-based**

T=250-350 °C → Nickel carbonyl formation

T=300-450 °C → Carbon formation

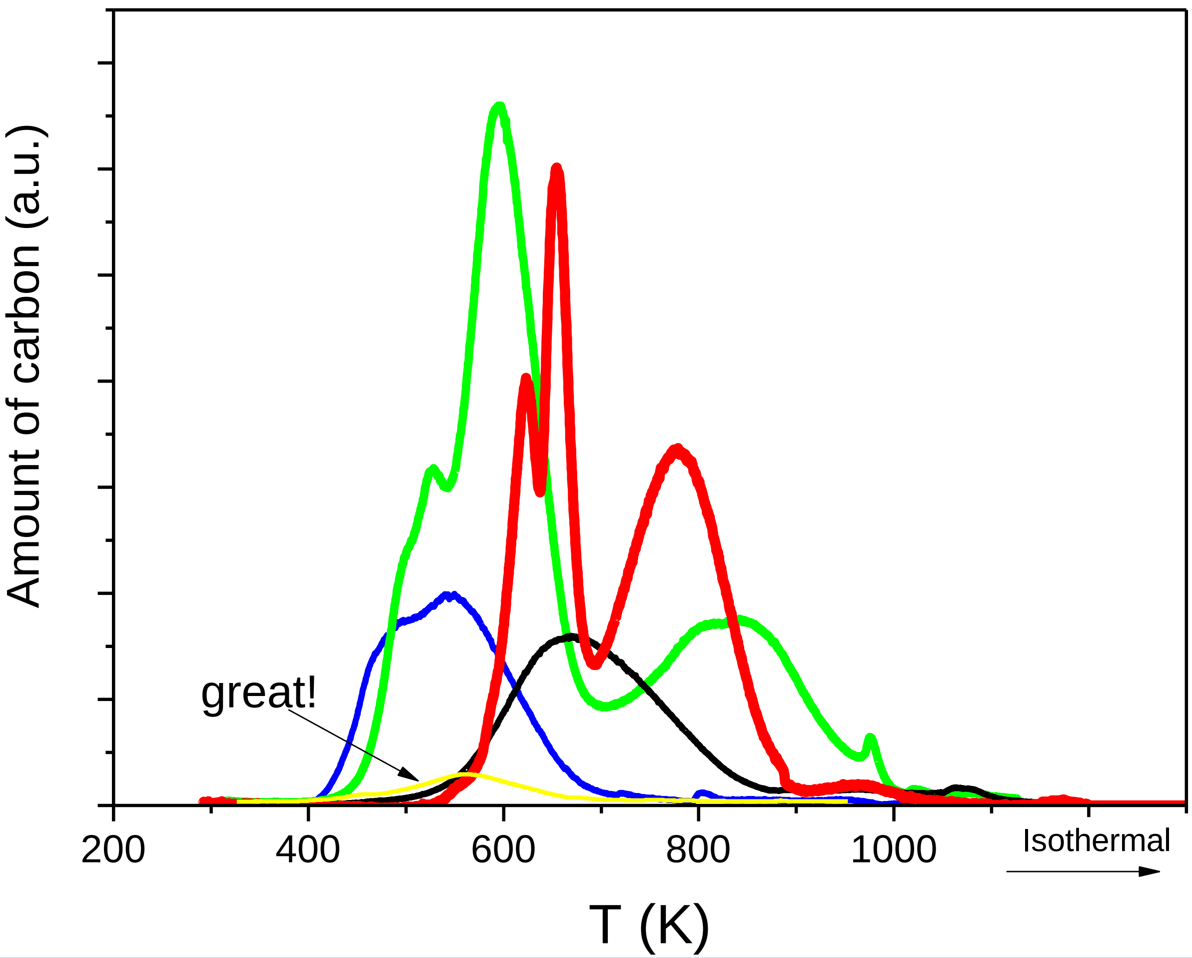
T=450-650 °C → Sintering

4. Methanation



Operating conditions: 20 bar, 310 °C and H_2/CO=3

4. Methanation



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Fuel From Waste

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