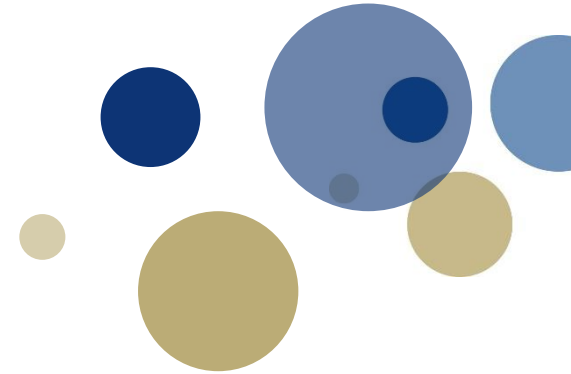**NTNU – Trondheim**
Norwegian University of
Science and Technology

**BIO4 FUELS**

# Gas conditioning and catalytic conversion

## Activities in Bio4Fuels WP4.2  and affiliated projects

## Edd A. Blekkan

*Catalysis group*
*Department of Chemical Engineering*
*Norwegian University of Science and Technology (NTNU)*
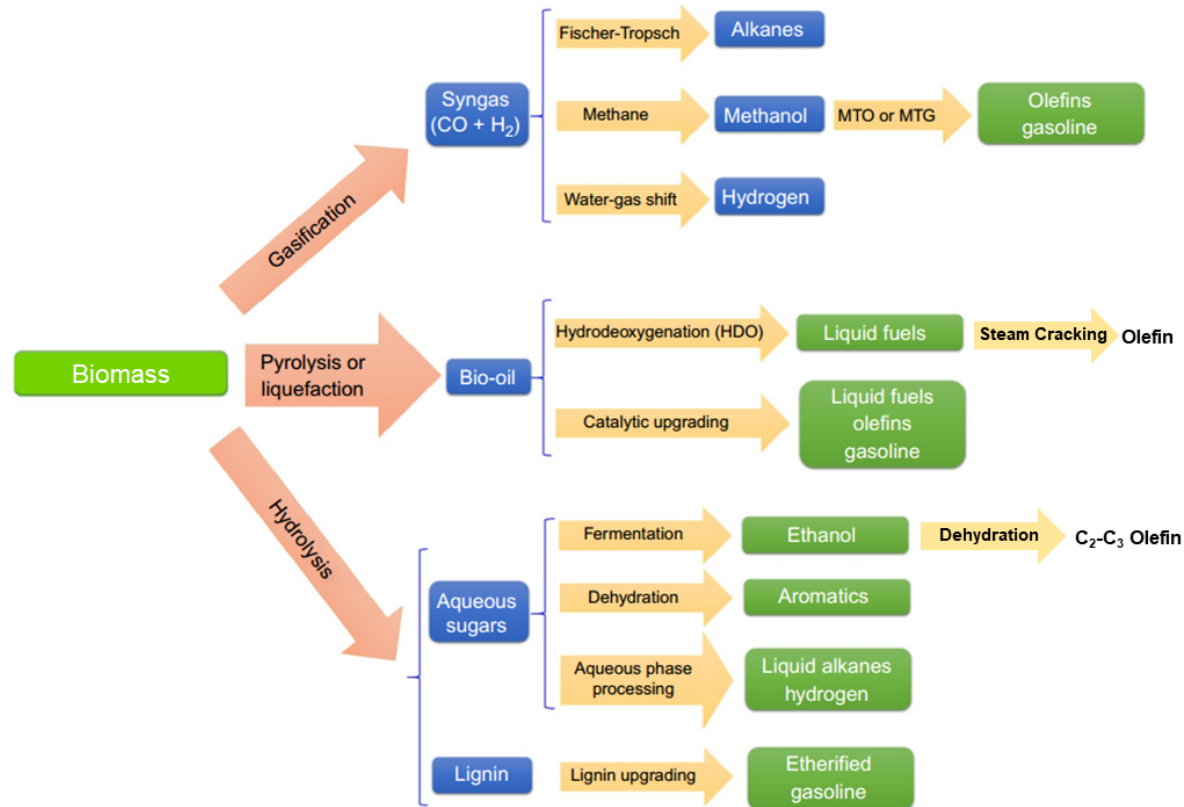*Trondheim, Norway*

*Bio4Fuels Days*
*Helsinki, Finland June12 - 13, 2024*

# Agenda:

**Examples from activities in the gasification value chain WP4.2 and associated projects**

- Introduction
- Gas conditioning
  - 1. Syngas cleaning; HTSS (High-Temperature Sulfur Sorbents)
  - 2. Tar reforming
- FTS
  - 1. Kinetics
  - 2. Poisoning studies
    - Phosphorous
- Summary

# Routes to biofuels



- 3 facets of a biofuels process:
  - Control molecular weight - fuels have specified boiling ranges adapted to engine technology
  - Control chemical composition – maximise heating value, control combustion properties
  - Remove oxygen – and at the same time maximise yields and efficiency
    - O out as $H_2O$ – costs hydrogen
    - O out as $CO_2$ – costs carbon
    - O left in the fuel molecules – lower heating value of the fuel
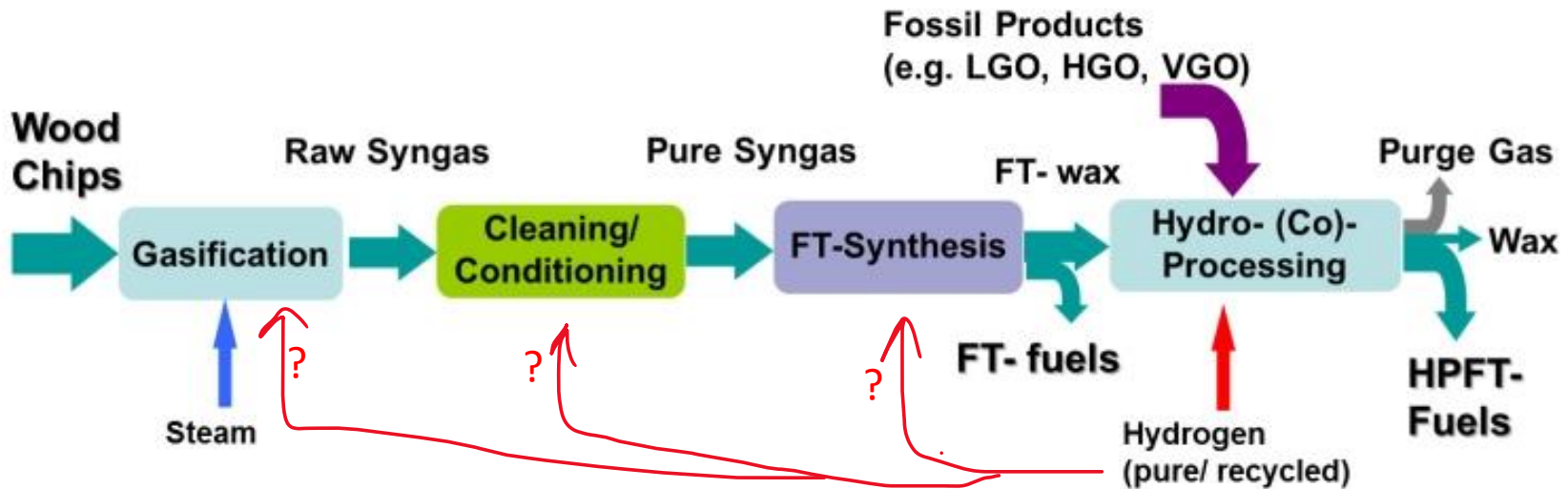
# Routes to biofuels
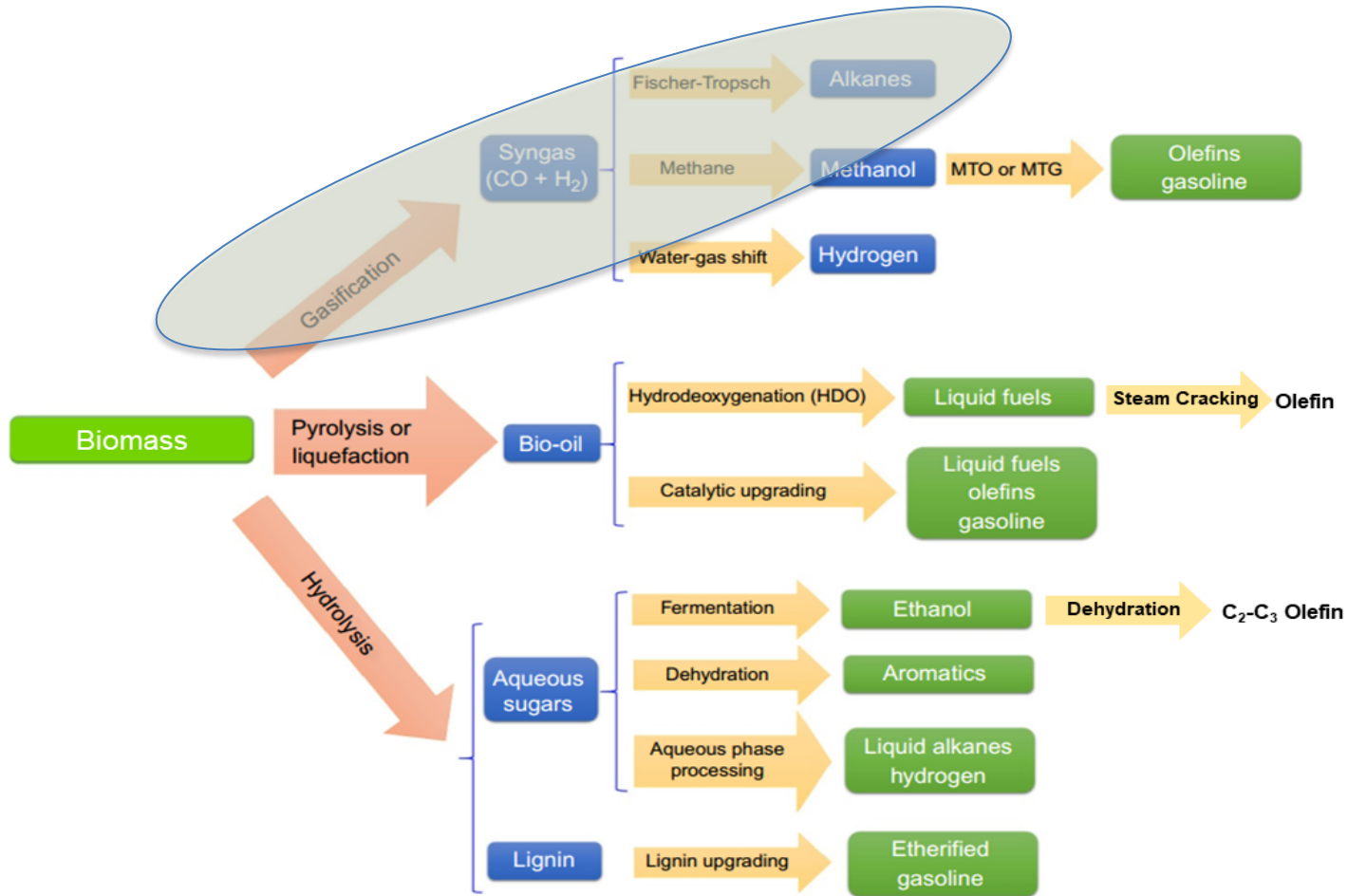
# Challenges
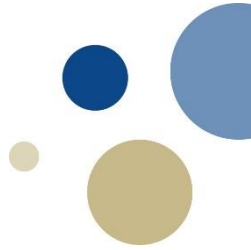
- Cost
  - Investment costs are high
  - Operational costs are high

- Efficiency
  - Energy losses in processing are too high
  - Loss of carbon in the process

- Feedstock supply
  - Availability
  - Costs of harvest, transport
  - Scale of operation issues

  ➔ Technology improvements are needed

# Plant design – many options



**Proposed BtL plant layout** (Boerrigter et al. *2nd World Conf. Technol. Exhib. Biomass Energy, Ind. Clim. Prot.* **2004**, 10–14)

- Gasification step determines composition
- Subsequent steps important for economy of the process
- Adding energy (heat, and/or $H_2$) will benefit efficiencies
  - See e.g Putta et al., Frontiers in Energy Research 9 (2022), 758149 doi: 10.3389/fenrg.2021.758149

# Agenda:
**Examples of activities in the gasfication  value chain**

- Introduction
- <span style="color:red">Gas conditioning</span>
  - 1. Syngas cleaning; HTSS (High-Temperature Sulfur Sorbents)
  - 2. Tar reforming
- FTS
  - 1. Kinetics
  - 2. Poisoning studies
    - Alkali
    - Phosphorous
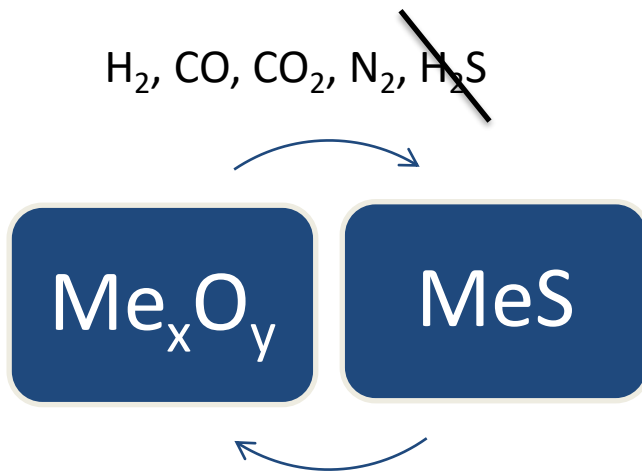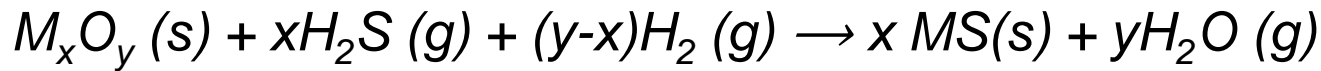- Summary

# Gas conditioning 1. Gas cleaning

- Feedstock impurities
- Biomass is «dirty»
  - Contains inorganic materials, sulfur, ash – needs removal before catalytic stage
- Gas cleaning is important part of syngas-based processes
  - State of the art:
    - Rectisol, Selexol – gas must be cooled to below 0 °C
    - Sulfur capture using Zn-based sorbents: not applicable at high T, large volumes needed
  - High cost (CAPEX & OPEX)
- Solid sorbent at high T (HTSS)
  - Avoid cooling – reheating syngas
  - Avoid solvent use and handling
  - Sorbent can be regenerated – reduce reactor volume
- Process requirement: < 1 ppm S

| Application | Allowable Sulphur levels (ppmv) |
|---|---|
| Ammonia production | <0.1 |
| Methanol synthesis | <1 |
| Solid oxide Fuel cell | <9 |
| Phosphoric acid fuel cell | <50 |
| Molten Carbonate fuel cell | <0.5 |
| Fischer-Tropsch synthesis | <1 |
| Gas turbines | <100 |

*Hofbauer, H.; Rauch, R.; Bosch, K.; Koch, R.; Aichernig, C.; Biomass CHP Plant Güssing – A Success Story, Expert Meeting on Pyrolysis and Gasification of Biomass and Waste; October 2002, Strasbourg, France*

# High temperature desulphurization using regenerable solid sorbents

$$M_xO_y \ (s) + xH_2S \ (g) + (y\text{-}x)H_2 \ (g) \longrightarrow x \ MS(s) + yH_2O \ (g)$$

$H_2$, CO, $CO_2$, $N_2$, $H_2S$

$Me_xO_y$ $\longrightarrow$ MeS

Regeneration agents: $O_2$, $SO_2$, $H_2O$

Candidate metals: Zn, Cu, Ca, Fe, Mn

**Requirements:**
- High equilibrium constant and fast kinetics for the sulfidation reaction
- High selectivity towards sulfur capture to minimize side reactions;
- Resistance to reduction by $H_2$ or CO
- High mechanical stability
  - Especially if used in moving or circulating beds
- Good regeneration capabilities
  - Sulfate formation is unwanted

# New sulfur sorbent: Mn-Mo/Al$_2$O$_3$



(A)



(B)
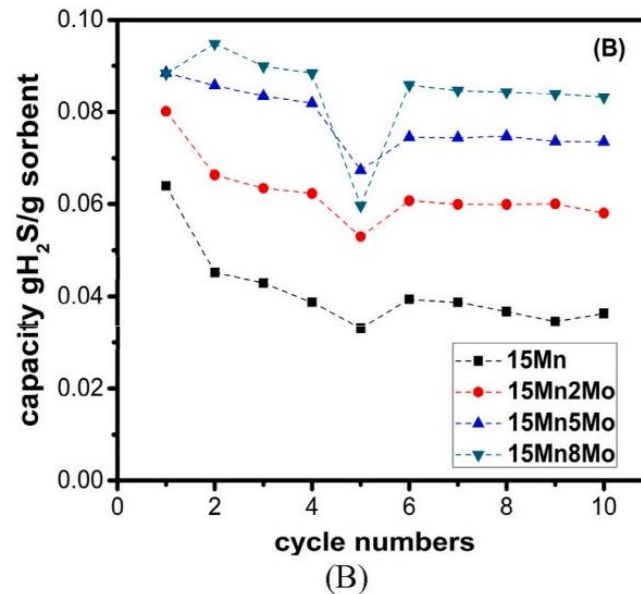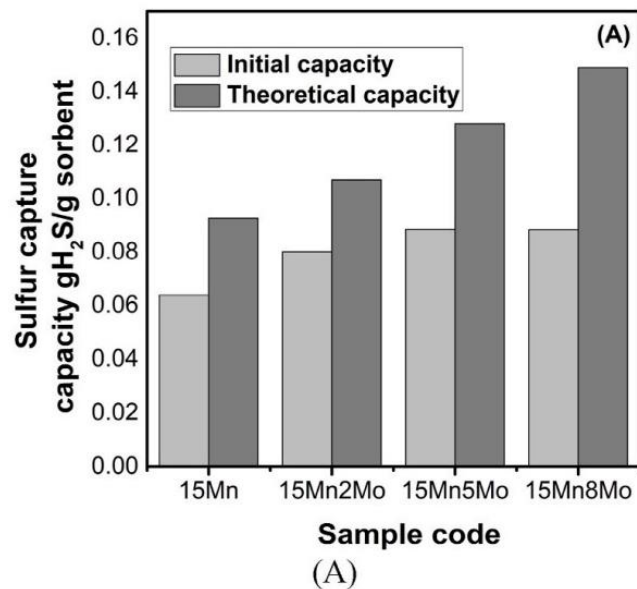
- Graphs show cyclic tests in dry conditions
  - A: Theoretical capacity: Mn and Mo oxides converted to sulfides
  - B: Stability over 10 cycles
- Supported material provides high rates and efficient utilization of the active phase
  - Small Mn-oxide particles, high surface area
- Mo promotion increases capacity and stability
  - Formation of mixed oxide MnMoO$_4$, stabilizing the structure
- Sorption chemistry complicated by oxidation of H$_2$S to SO$_2$

# Sub-ppm levels achieved
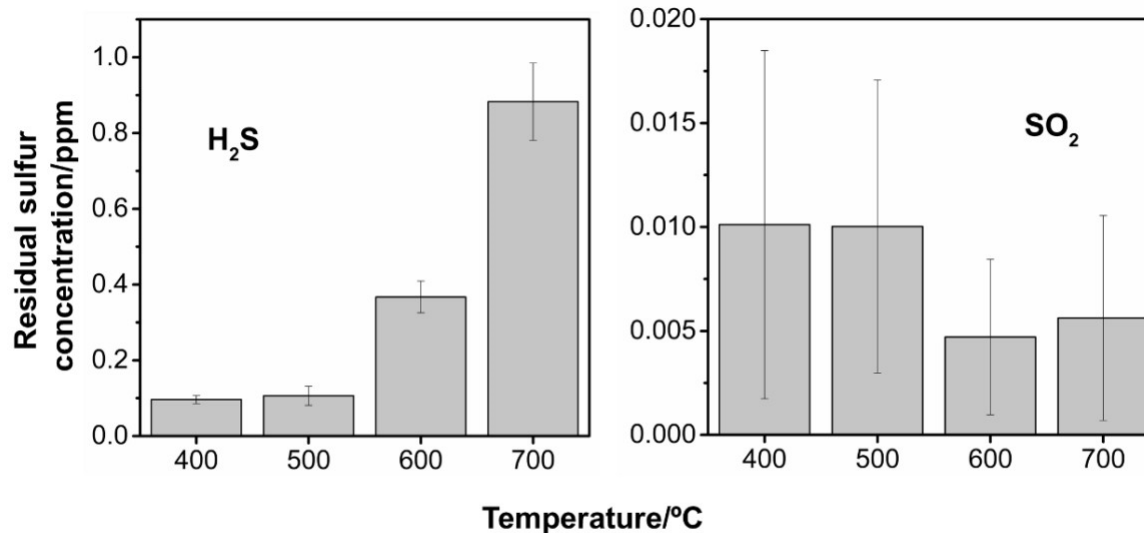


**Figure 2.** Residual sulfur concentrations measured at various temperatures with sorbent 15Mn8Mo with the gas compositions 0.2, 19.8, 40.0, and 40 vol.% for $H_2S$, Ar, $H_2$, and $N_2$ (2000 ppm $H_2S$) and 60,000 $mL_{gas}/g_{sorbent}$ h space velocity.

- Sub-ppm levels in dry conditions
- Minimal $SO_2$ formation due to oxidation of $H_2S$ by oxides
- $SO_2$ formation limited by pre-reduction of sorbent

Ma *et al.*, Reactions Vol 2 (2021), 365–373.

# Effect of steam (2000 ppm H$_2$S) 15Mn8Mo/Al$_2$O$_3$ sorbent, 600 °C
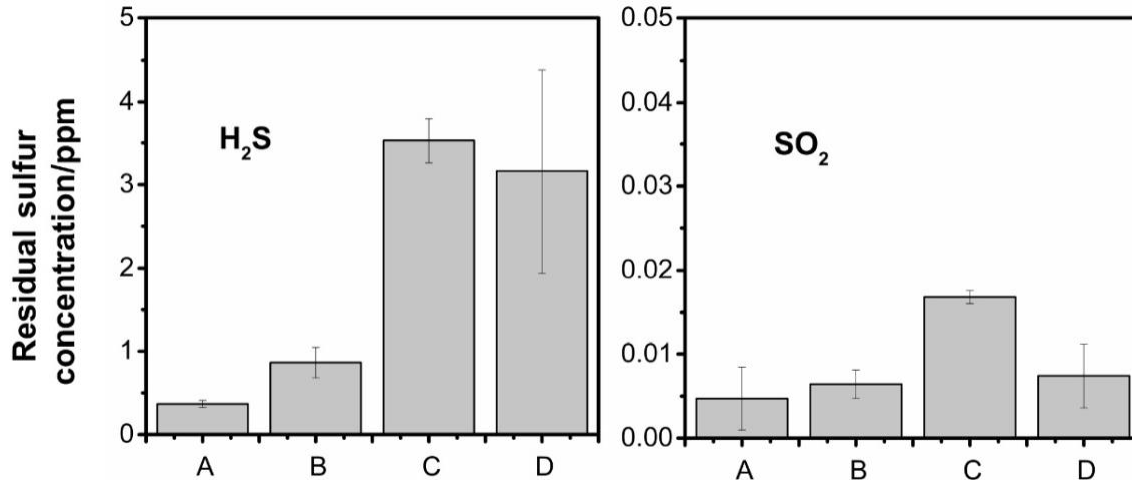
Conditions:
A: Dry, 60000 hr$^{-1}$
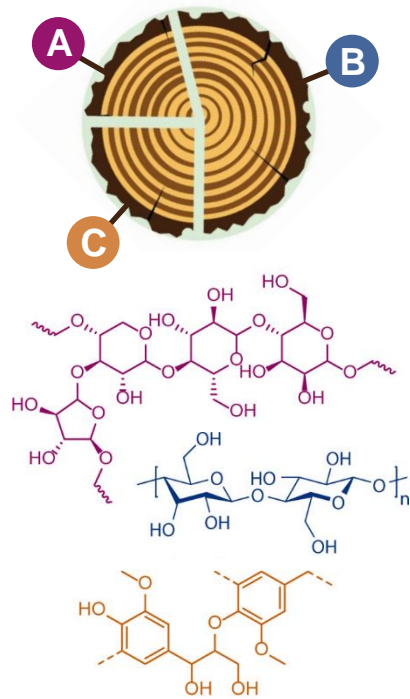B: 6,5% steam, 30000 hr$^{-1}$
C: 6,5% steam, 60000 hr$^{-1}$
D: 6,5% steam, 60000 hr$^{-1}$
 (doubled linear gas
 flow rate)

- Steam inhibits sulfur uptake but very low levels still attainable

Ma et al., Reactions Vol 2 (2021), 365–373.

# Gas conditioning  2. Tar reforming



A: Hemicellulose (10-40%), B: Cellulose (40-60%), C: Lignin (15-30%)

700-1600 °C
$H_2O/O_2$/air

**Syngas**

$H_2$ + CO

**Gas impurities:** $CO_2$ + $CH_4$ + $C_2H_x$

**Solid inorganics (ash):** $Na_2O$ + $K_2O$ + MgO + CaO + $SiO_2$ + $P_2O_5$ + $SO_3$ + $Al_2O_3$ + $Fe_2O_3$
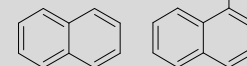
**Volatile inorganics:** $NH_3$ + HCN + $H_2S$ + HCl

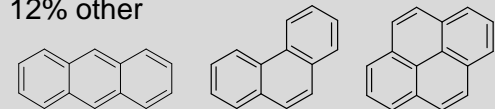**Tars (condensable hydrocarbons):** 10 g/$Nm^3$

66% one-ring
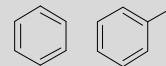
17% two-ring

5% phenol

12% other

Stevens, D. J.; tech. rep. NREL/SR-510-29952; National Renewable Energy Laboratory, U.S. Department of Energy, 2001.
Milne, T. A.; *et al.*; tech. rep. NREL/TP-570-25357; National Renewable Energy Laboratory, U.S. Department of Energy, 1998.

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# Basic chemistry repetition

**Table 5.2** Reactions during methane conversion with steam and/or oxygen.

| Reaction | $\Delta_r H_{298}$ (kJ/mol) |
|---|---|
| $CH_4 + H_2O \rightleftarrows CO + 3\,H_2$ | 206 |
| $CO + H_2O \rightleftarrows CO_2 + H_2$ | −41 |
| $CH_4 + CO_2 \rightleftarrows 2\,CO + 2\,H_2$ | 247 |
| $CH_4 \rightleftarrows C + 2\,H_2$ | 75 |
| $2\,CO \rightleftarrows C + CO_2$ | −173 |

In addition: tar conversion

$C_xH_y + xH_2O = xCO + (x+y)/2\,H_2$

- Heavier hydrocarbons are very reactive, at methane reforming conditions ➔ coke formation
- Usually converted to $C_1$ ($CH_4$ & CO) in pre-reformer
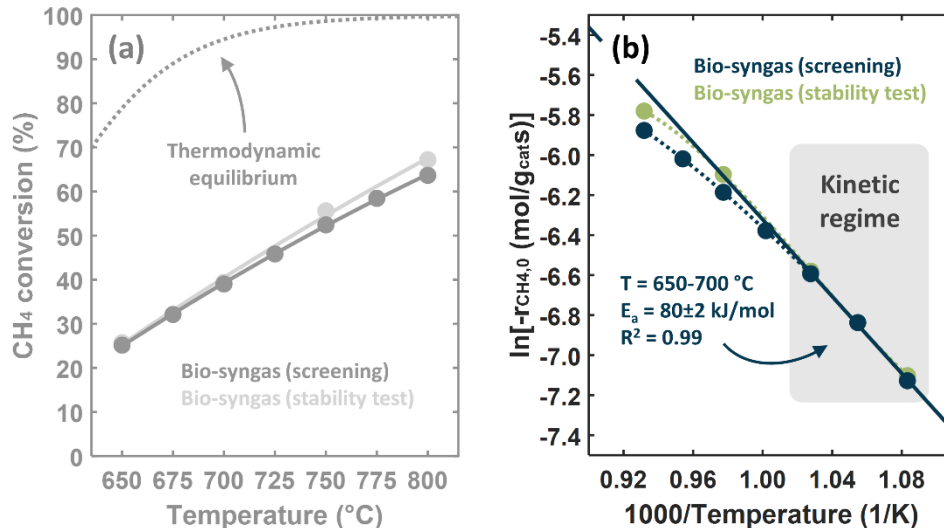
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# Model syngas reforming



Figure: S/C = 3.0, GHSV = 85000 NmL/$g_{cat}$min, Tar free conditions, Catalyst = 20-20 wt% Ni-Co/Mg(Al)O

**Methane conversion as marker for activity, kept low to observe effects**

**Tar conversion always complete**

**Temperature screening:**

High GHSV targeting low conversion

Approach to equilibrium < 50% at lower temperatures (650-725 °C)

Experimental repeatability demonstrated

**Intrinsic kinetics:**

Linear Arrhenius plots at lower temperatures (650-700 °C)

Activation energies (75-89 kJ/mol) close to expected values

# Catalyst for tar reforming: 20-20 wt% Ni-Co/Mg(Al)O

**Bio-syngas (tar free):**

Linear decay model: $y = 1 + A \cdot TOS$

Coke free operation
Deactivation by sintering/oxidation

**Bio-syngas + Tar:**

Exponential + linear decay model:
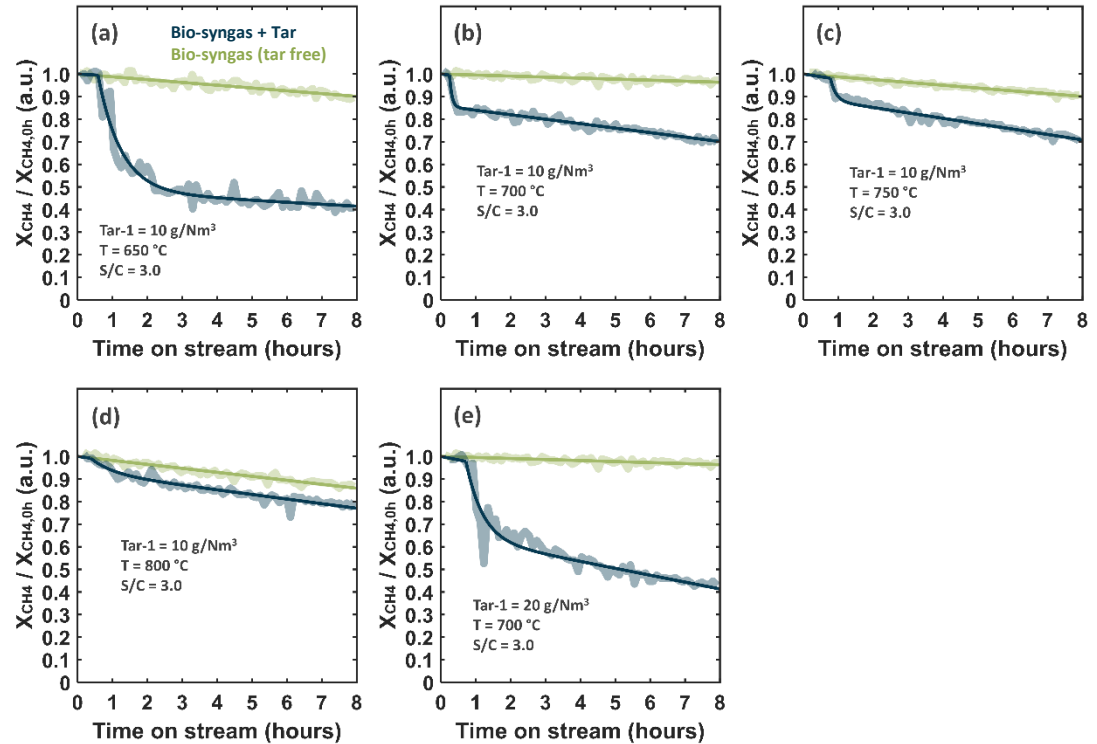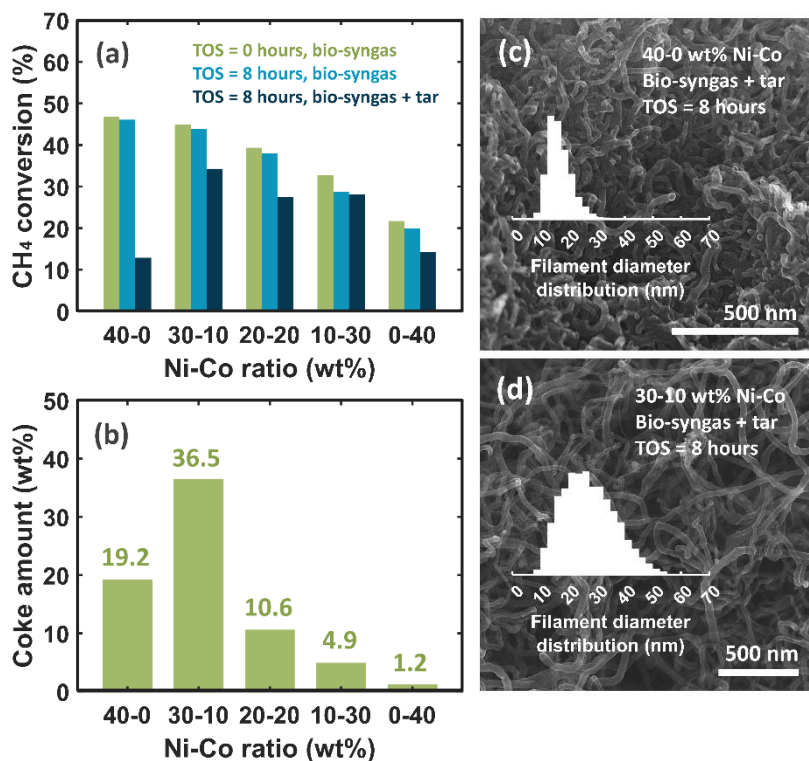$y = 1 + A \cdot TOS + C \cdot \exp(-D \cdot TOS)$

Considerable coke formation



Figure: T = 650-800 °C, S/C = 3.0, GHSV = 85000 NmL/$g_{cat}$min,
Tar = 10-20 g/Nm$^3$ toluene, Catalyst = 20-20 wt% Ni-Co/Mg(Al)O

# Coke formation is a key issue



**Ni sample:** Strong deactivation effects as expected from previous literature

**30-10 wt% Ni-Co:** Deactivation reduced at the expense of enhanced carbon filament growth

Shifted filament diameter distribution

Changing filament growth threshold and/or metal particle size selectivity?

**Low Ni-Co ratios:** Coke formation reduced at expense of initial catalyst activity

**Conclusion:** Strong Ni-Co synergy effects

Intermediate Ni-Co ratio provides compromise of coke formation resistance and initial activity

Figure: T = 700 °C, S/C = 3.0, GHSV = 85000 NmL/$g_{cat}$min, Tar = 10 g/$Nm^3$ toluene, Catalyst = Ni/Mg(Al)O / Ni-Co/Mg(Al)O / Co/Mg(Al)O. (c-e) STEM (>1000 filaments measured).

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# Coking is inevitable?
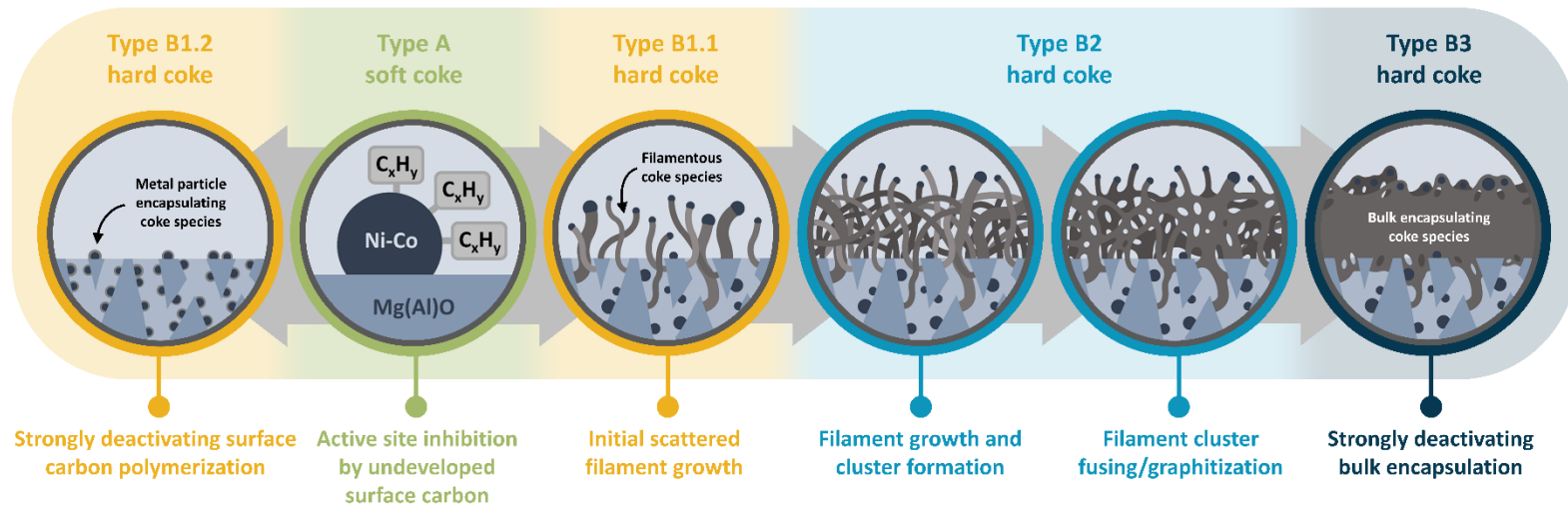


- Coke is difficult to avoid
- Different types identified
- Regeneration will be necessary?
  - Coke burning undesired?
  - Coke removal «in situ» in clean syngas?
    - Possible if coke load is limited

# 2.5 Switch-SRCG dual-bed design

**Initial regeneration experiments:**

1) Coke formed through first hours on stream are effectively removed in the tar-free bio-syngas

2) Efficient tar elimination → Tar-free bio-syngas

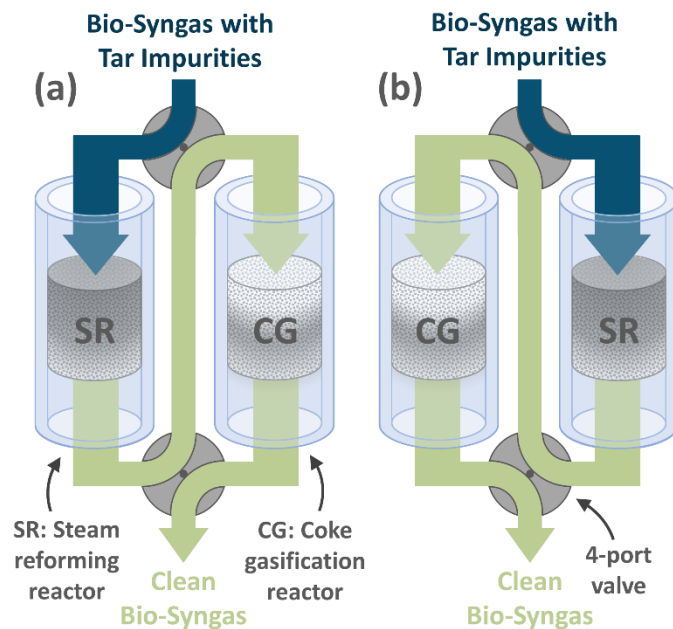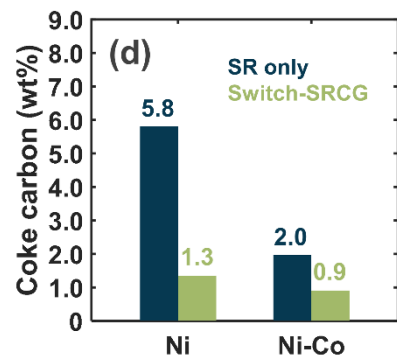3) Carbon on catalyst is controlled:





Figure: Switch-SRCG dual-bed design. Catalyst cycle between steam reforming (SR) and downstream regeneration by coke gasification (CG) in tar free bio-syngas.

# Agenda:
## Examples of activities in the gasfication  value chain

- Introduction
- Gas conditioning
  - Syngas cleaning; HTSS (High-Temperature Sulfur Sorbents)
  - Tar reforming
- FTS
  - Kinetics
  - Staging
  - Poisoning studies
    - Alkali
    - Phosphorous
- Summary

# Key features of the FTS reaction (over cobalt catalysts)

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

- Polymerization mechanism, chain growth probability α determines product distribution with 2 exceptions
  - More $CH_4$ than predicted
  - Less (almost no) $C_2$ than predicted
- One water molecule produced per CO incorporated in the chain
  - Water *enhances or decreases catalyst activity* depending on catalyst formulation and water pressure level
  - Water ALWAYS *increases selectivity* to higher hydrocarbons ($C_{5+}$ or ASF α)

$$\alpha = r_p/(r_t + r_p)$$

  - Water *contributes to deactivation*
    - *Sintering, re-oxidation of small Co particles*

# How we study FTS
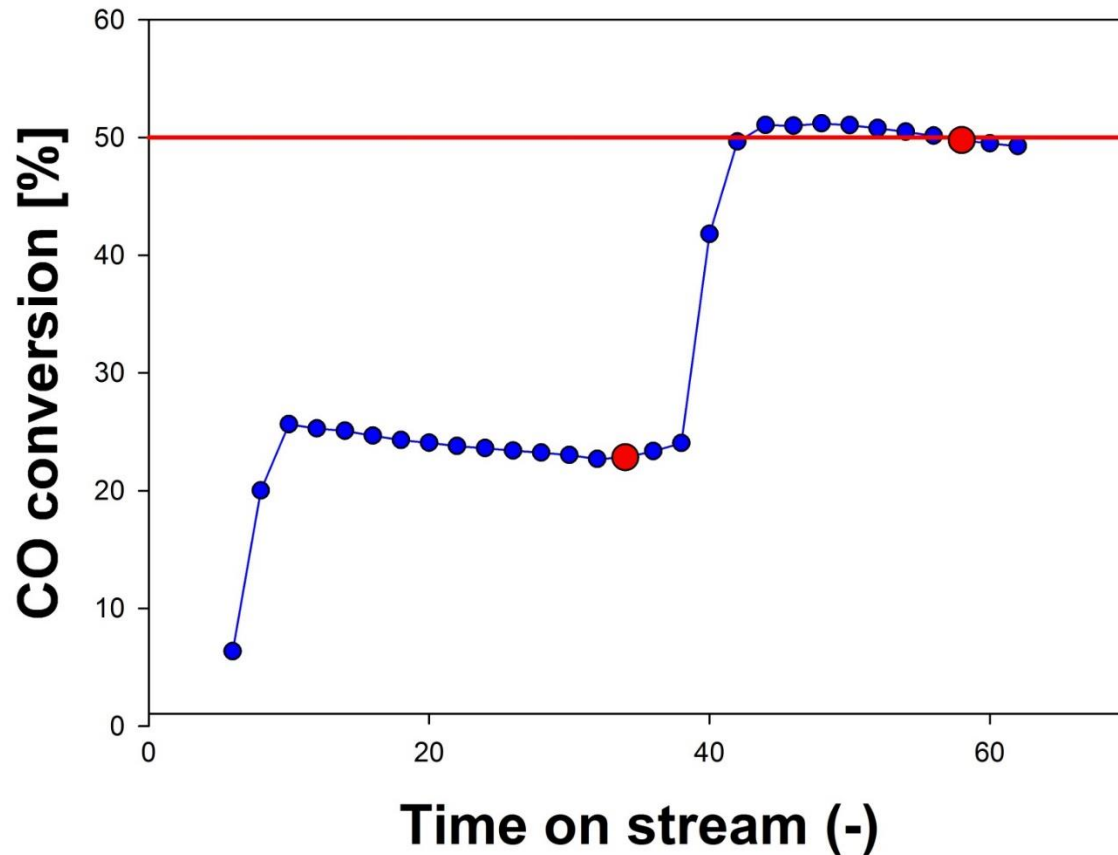


- Tubular micro-reactor (pfr), catalyst diluted with inert (SiC)
- Pre-reduction (cobalt: typically 350 °C, 1 bar $H_2$)
- Relevant P, T and SV
- Controlled start-up of the experiment (to avoid temperature run-away)
- Fixed flow-rate for 24h (activity data)
- Adjust feed rate to obtain 50% conversion (Selectivity data)

# Main reason:
# $C_5^+$ Selectivity increases with $P_{H_2O}$



Chart: $C_5+$ selectivity [%] vs Partial pressure of water [bar]

$$nCO + 2nH_2 \rightarrow [CH_2]_n + nH_2O$$
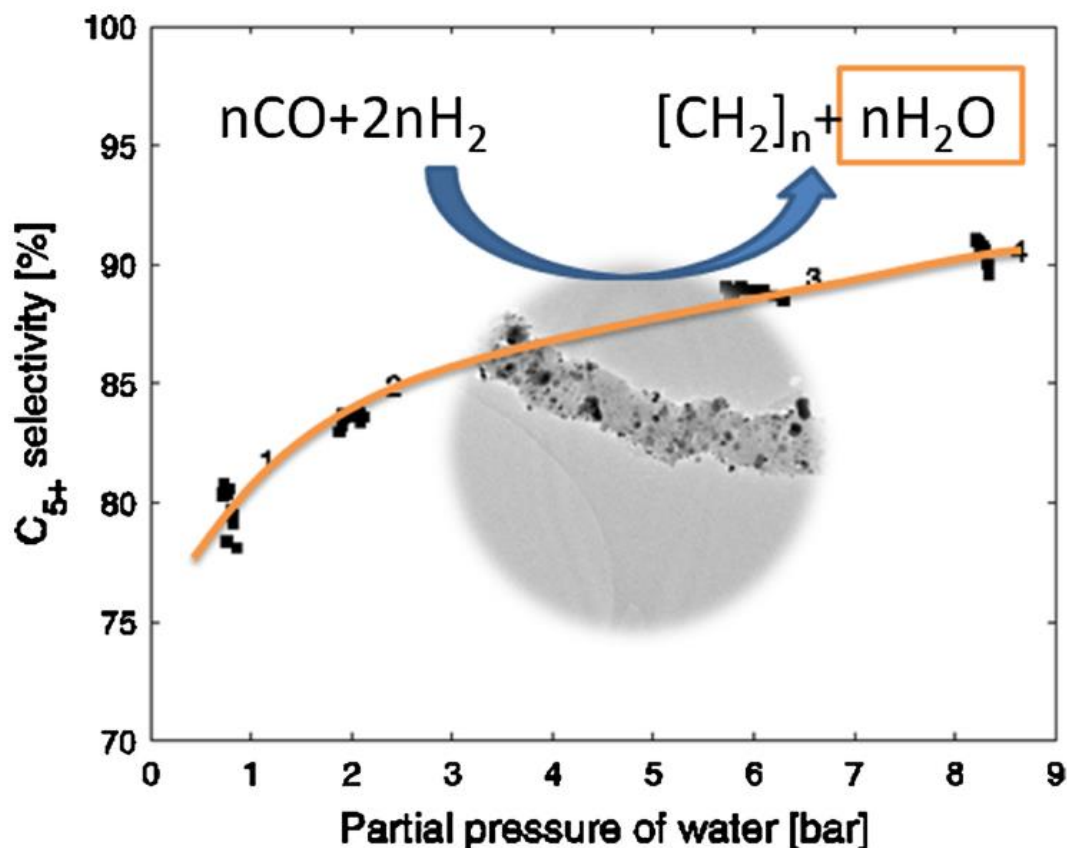
- Example: Co/CNF
  - 20%Co/CNF (inset TEM image)
  - IW impregnation of purified platelet CNF
  - $S_g = 117$ m$^2$/g
  - $D_{Co} = 5.4\%$
    - (18 nm Co particles)
  - FTS at 483 K, 20 bar, $H_2$:CO = 2:1.

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# FTS 1. Kinetics and process studies
## (Co-based catalyst for liquid hydrocarbon synthesis)
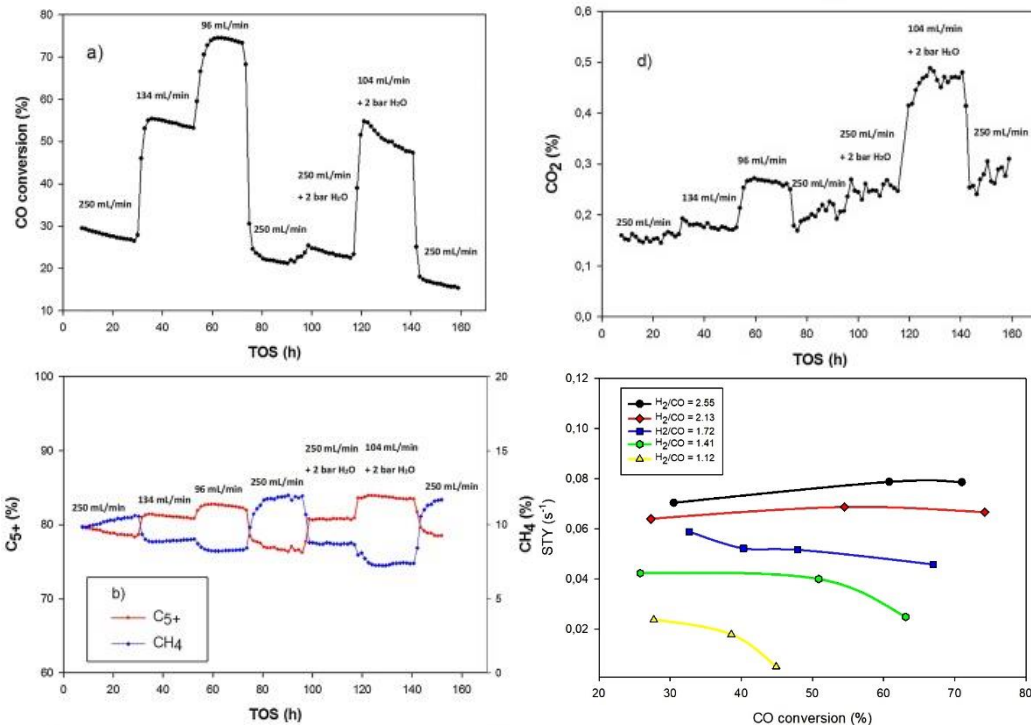


- Cobalt FTS is sensitive to conversion
  - Catalyst activity
  - Liquid selectivity
- Usage ratio is > 2
- Deactivation
- WGS activity

- Can we capture this in a model?

# Kinetic model developed

- FT rate:

$$r_{FT} = \frac{k p_{CO} p_{H_2}^{1/2} (1 + k_{p_{H_2O}} p_{H_2O})}{\left(1 + a' p_{CO} + b p_{H_2}^{1/2} + f' p_{H_2O}\right)^2}; \quad k_{p_{H_2O}} = 0.1 \text{ MPa}^{-1}$$

- Chain growth:

$$\alpha = \frac{1}{1 + k_\alpha(T_k) \dfrac{1}{p_{CO}^z p_{H_2O}^y}} \qquad \text{where} \qquad k_\alpha = k_{\alpha,\text{ref}} e^{-\frac{E_a^\alpha}{R}\left(\frac{1}{T_k} - \frac{1}{483}\right)}$$

- WGS

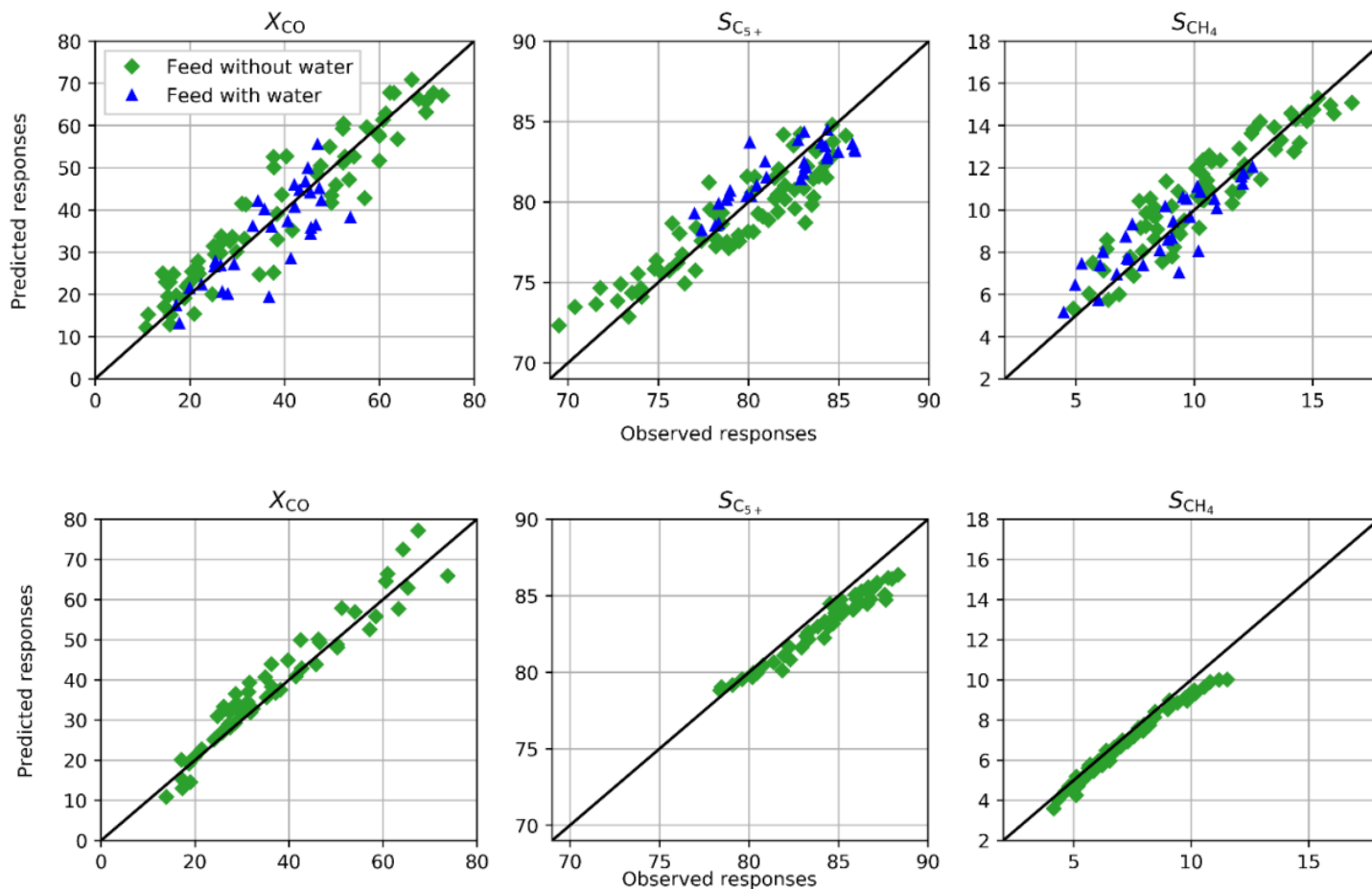$$r_{WGS} = k_{CO_2} \left( p_{CO} p_{H_2O} - \frac{1}{K_{eq}} p_{CO_2} p_{H_2} \right)$$

- Deactivation

$$\frac{da}{dt} = -k_{\text{deact}} p_{H_2O}^\gamma a^n; \quad n = 2 \text{ and } \gamma = 1$$

**Parity plots**
**Top: data used in model development (Todic et al.)**
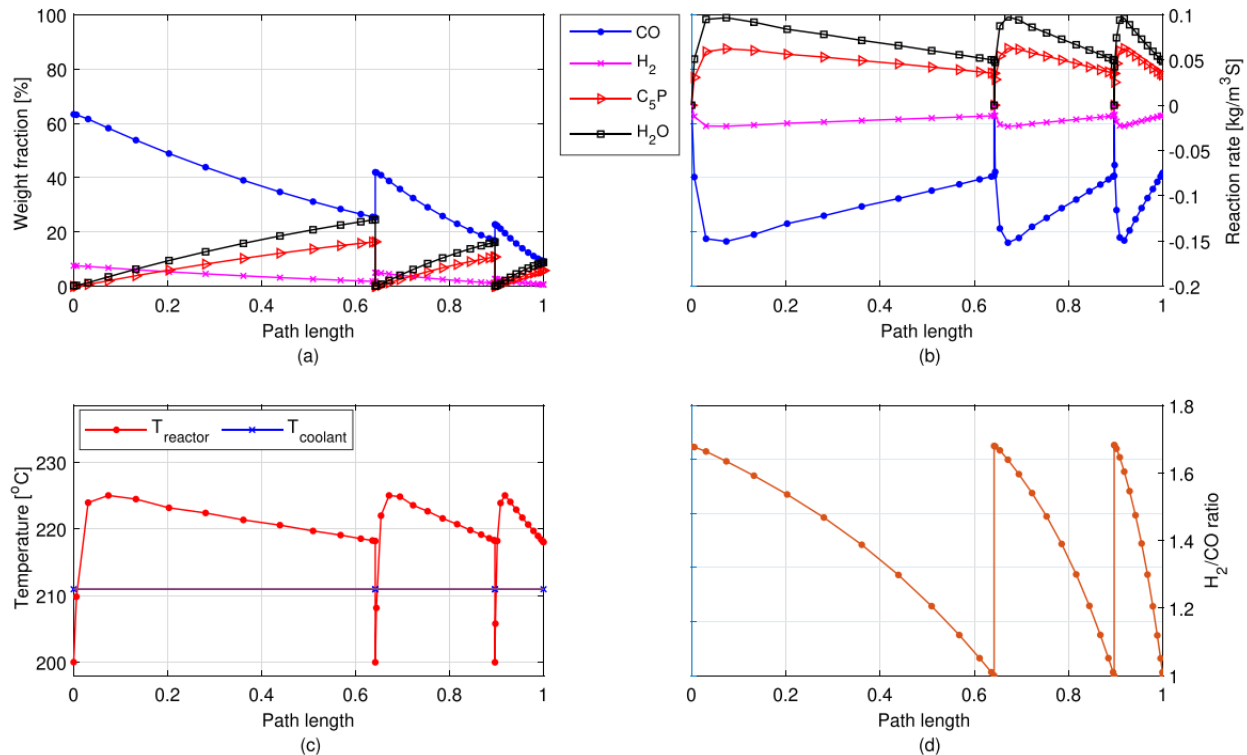**Bottom: Validation (Gavrilovic et al. )**

# Model application:
## Optimized design of multi-stage process



a) Mass flows
b) Reaction rates
c) Temperature
d) $H_2$:CO ratio

- Optimal volume distribution between stages found
- Maximized $C_5^+$ gives highest revenue
- $H_2$:CO ratio best kept as low as possible (added $H_2$ between stages)
- Low T beneficial for high $C_5^+$

# FTS 2. Phosphorous poisoning

- Significant concentrations of P in biomass, wastes etc.
- P as a catalyst poison not much studied
  - Need knowledge to define syngas requirements, purity
- This study done at «olefin-favoring» conditions
  - Mn-promoted catalyst
  - Lower operating pressures (5-10 bar)
  - Higher operating temperature (240 °C

- Catalyst poisoned by impregnation
  - Co catalyst promoted by Re and Mn  (higher olefin selectivity)
  - Support effect studied ($Al_2O_3$, $SiO_2$, $TiO_2$)
  - 2 levels investigated
    - 1700 ppm P
    - 6700 ppm P

# Results: Catalytic testing. Activity measurements

**CO Conversion and Site Time Yield (STY)**

All catalysts remained stable for the first 24

Reduced CO Conversion and STY[1] with increased P loading

Different behavior in poisoned catalysts:

- More poisoning effect for $SiO_2$
- P might interact more with $Al_2O_3$ and $TiO_2$ than with cobalt compared with $SiO_2$
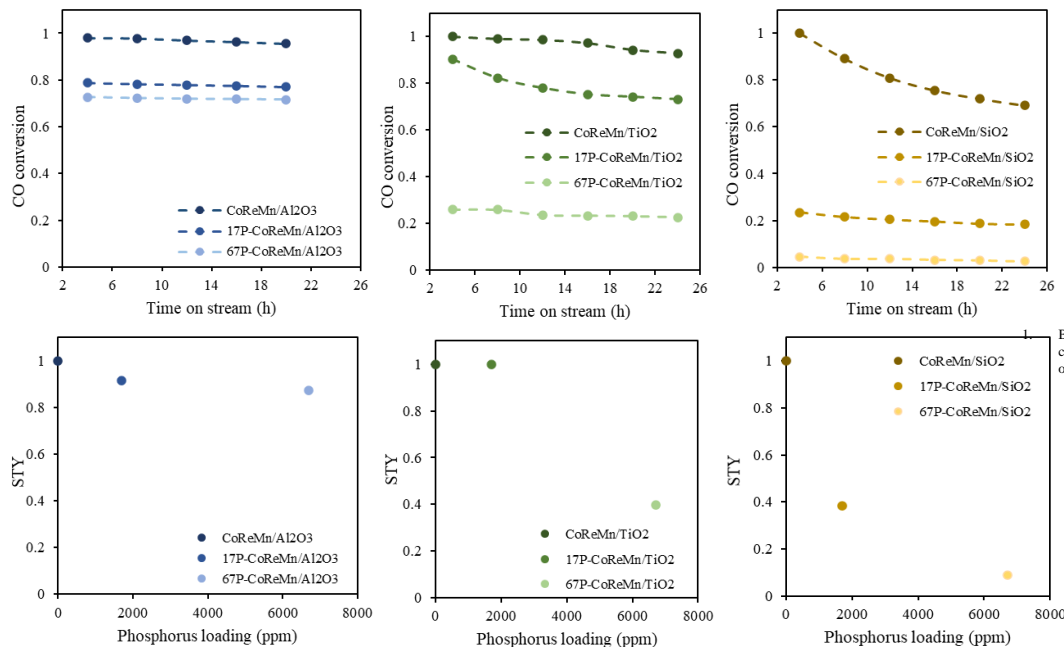- Metal-support interactions $Al_2O_3 > TiO_2 > SiO_2$

➔ Complicated relationship between P and activity decrease

❑ Site blockage
  - ❑ 1 atom of P blocks more than 1 Co atom
❑ Electronic effects (weak CO bonds)
  - ❖ Electronegativity of P



[1] Based on $H_2$ chemisorption

| | CoReMn/$Al_2O_3$ | 17P-CoReMn/$Al_2O_3$ | 67P-CoReMn/$Al_2O_3$ | CoReMn/$TiO_2$ | 17P-CoReMn/$TiO_2$ | 67P-CoReMn/$TiO_2$ | CoReMn/$SiO_2$ | 17P-CoReMn/$SiO_2$ | 67P-CoReMn/$SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| X $CO_{24}$ (%) | 51 | 40 | 36 | 29 | 22 | 7 | 23 | 7 | 1 |
| $STY_{24}$ ($s^{-1}$) | 0.48 | 0.44 | 0.42 | 0.58 | 0.58 | 0.023 | 0.34 | 0.13 | 0.003 |

Ivanez, Miro i Rovira & Blekkan, Catal. Today., in press (2024)

# Results: Catalytic testing. Selectivity measurements

## C5+ and Methane selectivity

**Selectivity compared at 50% of CO conversion**

- Reduction in $C_{5+}$ products
- Reduction in $C_{2-4}$ olefins
- Increase in $CH_4$ selectivity
- Increase in $C_{2-4}$ paraffins
- Increase in $CO_2$

**Increase in the rate of hydrogenation reactions**

**Reduction in the chain growth probability**
- Weak CO bonds
- Less reduced cobalt



Ivanez, Miro i Rovira & Blekkan, Catal. Today., in press (2024)
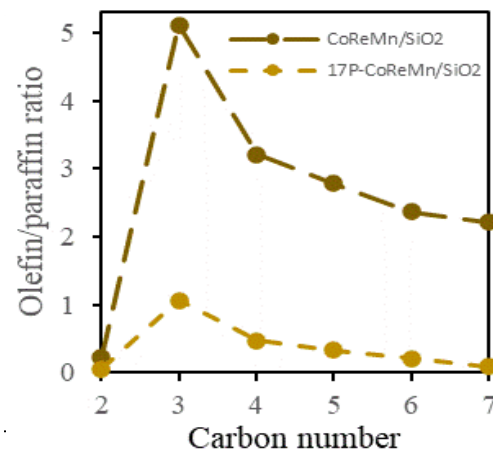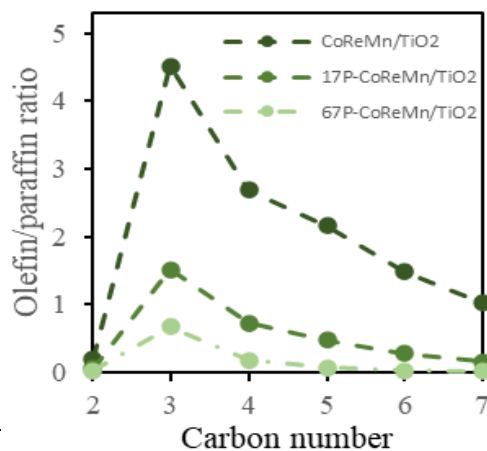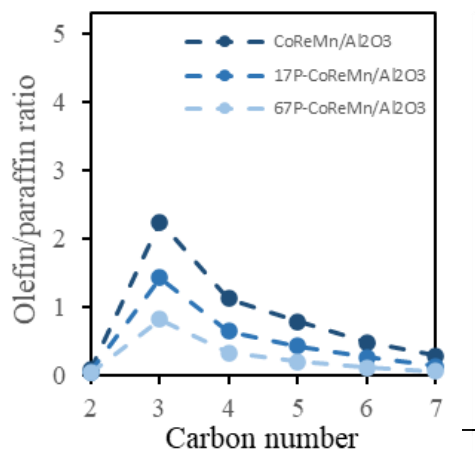
# Conclusion: Effect of Phosphorus

## Activity and selectivity

- Reduced CO conversion and intrinsic activity
- Higher hydrogenation activity

## Reducibility and desorption

- Reduction of reducibility
- Affect the $H_2$ desorption on $TiO_2$ and $SiO_2$

## Surface and chemical properties

- Small effect on surface area & porosity
- No cobalt-phosphorus species detected by XRD
- No effect on crystallinity of supports
- Minor decrease in measured metallic dispersion

1. Site blocking
2. Electronic effects
3. Higher adsorbed H to CO ratio

Increased effect $Al_2O_3 < TiO_2 < SiO_2$ (SMSI)
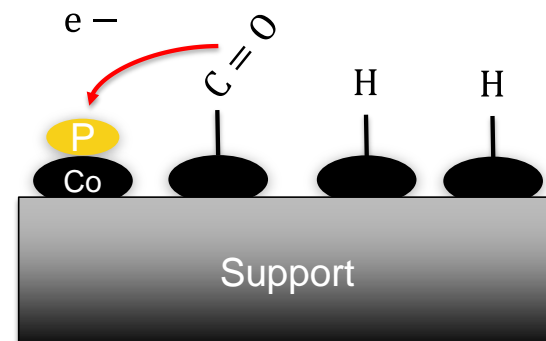
# **Summary**

- Large and broad activity over last 8 years
  - Many issues in the value-chain are visited

- Bio4Fuels activities and affiliated projects have been important in supporting research relevant for the gasification route

- Large number of candidates trained with background in relevant issues

# Thank you for your attention!

**Special thanks to PhD candidates, postdocs and master-students contributing to the projects:**

**PhD/postdocs:**
Ljubisa Gavrilovic
Jianju Ma
Ask Lysne
Oscar Ivanez Encinas
Umesh Pandey
Koteswara Rao Putta
Mehdi Mahmoodinia

**Master students**
Alicia San Martin
Ida Saxrud
Remi L.G. Snidaro
Anders Runningen
Erik A. Jørgensen
Anette S. Groven
Emma Birkeland
Kristin Øxnevad Madsen
Siri Stavnes
Jonas Save
Isabel Pascual García
Ida Uotila (VTT)

(Apologies to those forgotten!)

The rest of the catalysis group!