

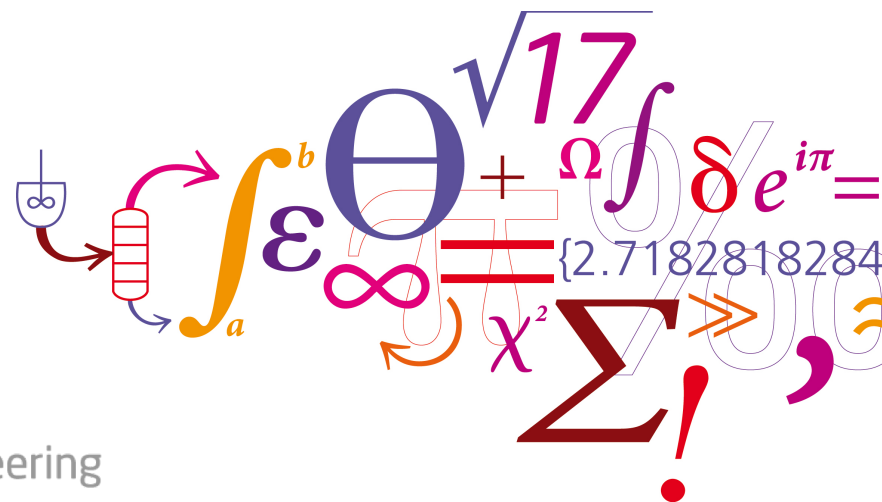
# Bio-refining with focus on Bio-manufacturing for SAF

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AT-CERE

Applied Thermodynamics - Center for Energy Resources Engineering



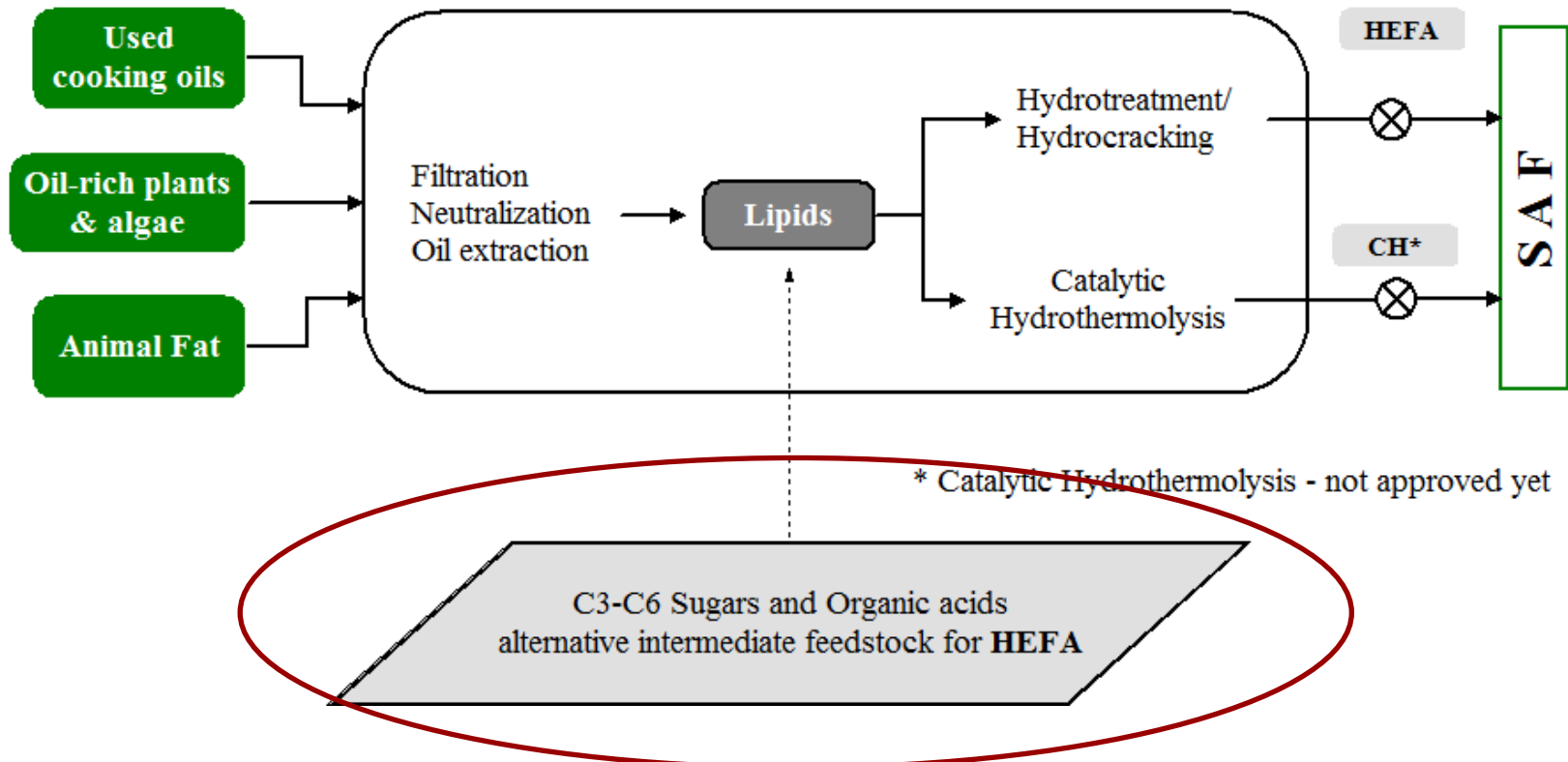
**DTU Chemical Engineering**

Department of Chemical and Biochemical Engineering

# Overview

- Microbial lipids as intermediate feedstock for HEFA pathway – coupled with lignin 1st biorefinery
- Coupling gasification and biochemical conversions for AtJ pathway
- CO<sub>2</sub> transformations with renewable H<sub>2</sub> in a highly efficient trickle bed reactor
- TRL of the technologies at DTU Chemical Engineering

# De-bottlenecking the HEFA pathway



- Limited availability of waste oils and oil crops in the Nordics
- Imported feedstock for the Nordics
- Forecasted heavy competition with the biodiesel industry – EU countries

# Microbial lipids

- Microbial lipids are accumulated intracellularly under conditions of unbalanced growth and serve as carbon and energy reserves for the cells
- Their technical profile is similar to plant oils and animal fat

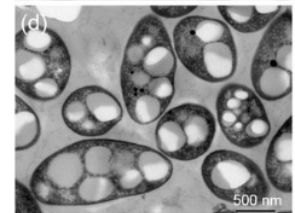


Table 7 Representative fatty acid composition of SCO produced by various oleaginous yeast strains and comparison to a number of technical oils

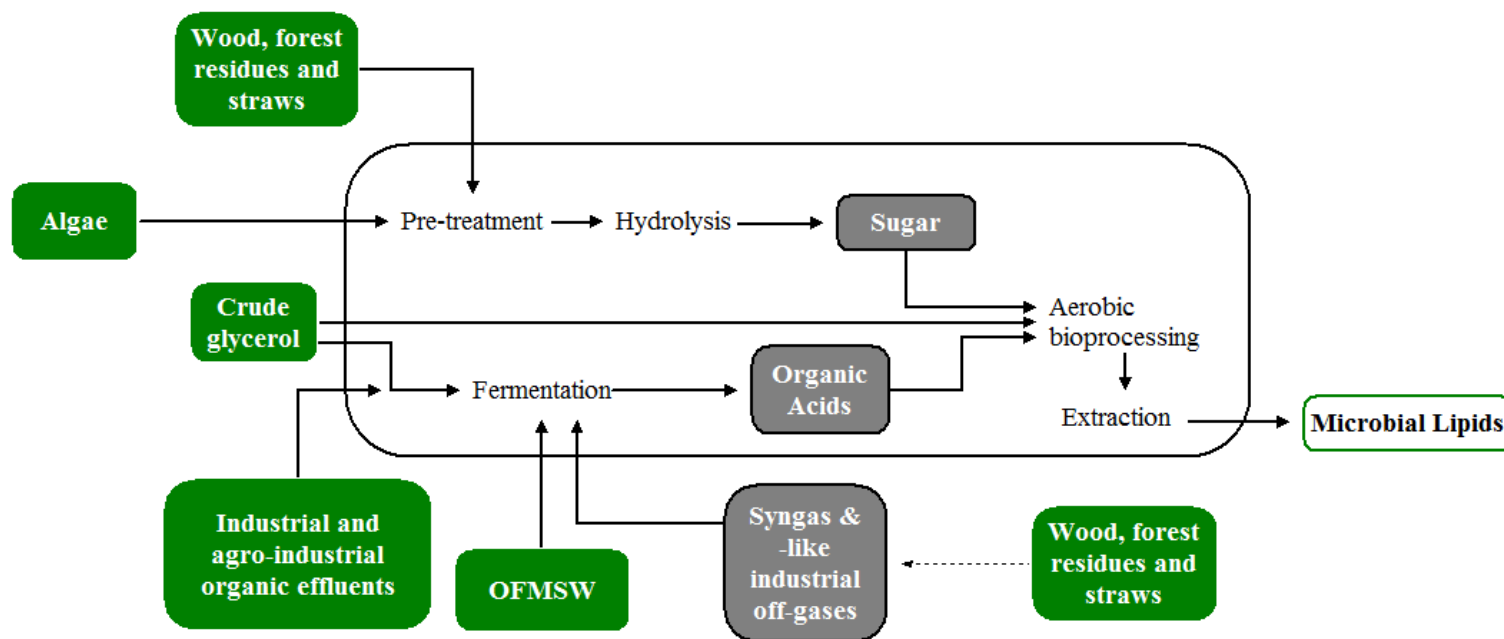
Microorganism	Total lipid content (% w/w)	Fatty acids (% w/w of total lipids)					Analogous (similar) technical profile
		C16:0	C16:1	C18:0	C18:1	C18:2	
<i>Candida curvata</i> D	58	32	—	15	44	8	Palm/Palm olein
<i>Candida</i> 107	42	44	5	8	31	9	Palm
<i>Cryptococcus albidus</i>	65	12	1	8	73	12	Olive oil
<i>Lipomyces starkeyi</i>	63	34	6	5	51	3	Palm/Palm olein
<i>Lipomyces starkeyi</i>	68	55.9	1.8	13.8	25.8	0.1	Cocoa butter
<i>Trichosporon pullulans</i>	65	15	—	2	57	24	Canola/olive
<i>Yarrowia lipolytica</i>	43	15	3	11	47	21	Chicken fat
<i>Rhodospiridium toruloides</i>	67.5	20	0.6	14.6	46.9	13.1	Lard

Koutinas et al., 2014, Chem.Sco.Rev. 43:2587



# Microbial lipids

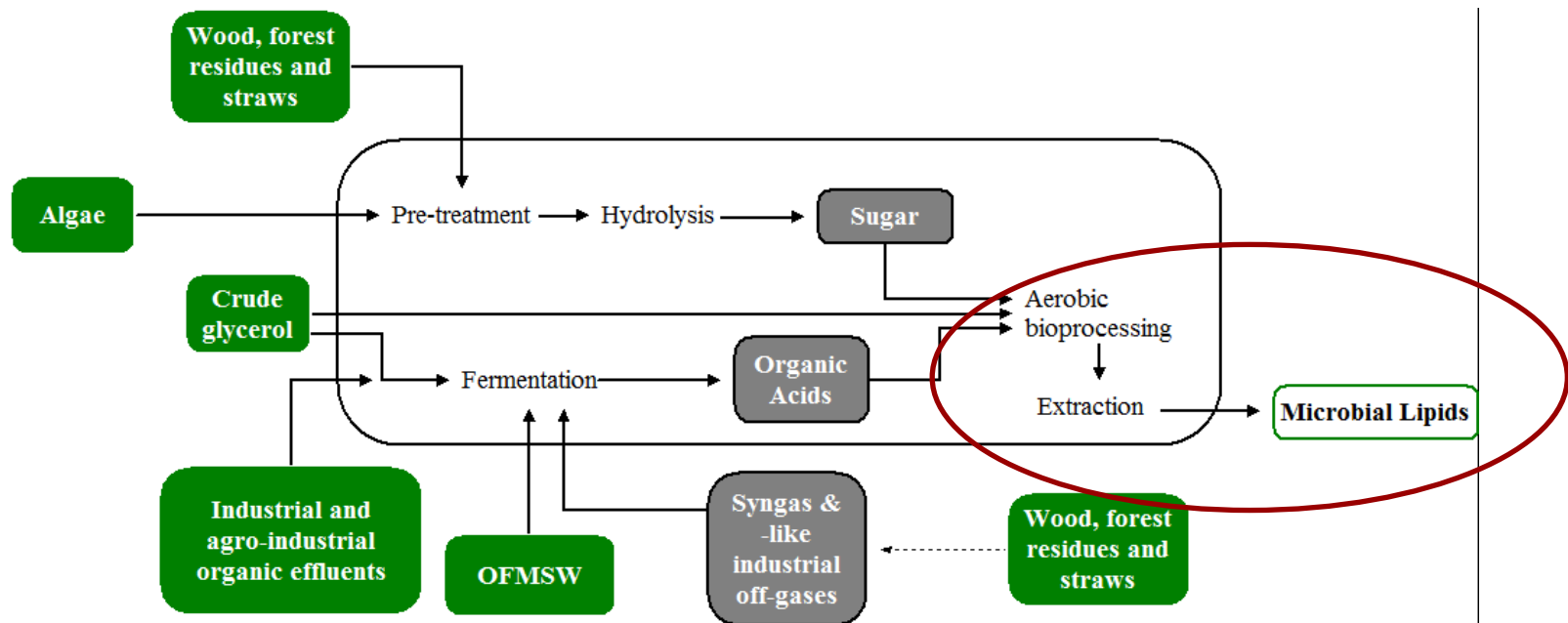
- Carbon source:  $C_3$ - $C_6$  sugars and lower molar mass organic acids as carbon sources
- Versatile feedstocks: lignocellulosic biomasses, municipal wastes, industrial and agroindustrial effluents rich in organic matter, crude glycerol and syngas



- Sugars and Organic acids-to-Lipids: TRL 3 internationally
- Lignocellulose-to-sugars: TRL 7 in DK BUT lignocellulosic sugars-to-lipids is currently investigated

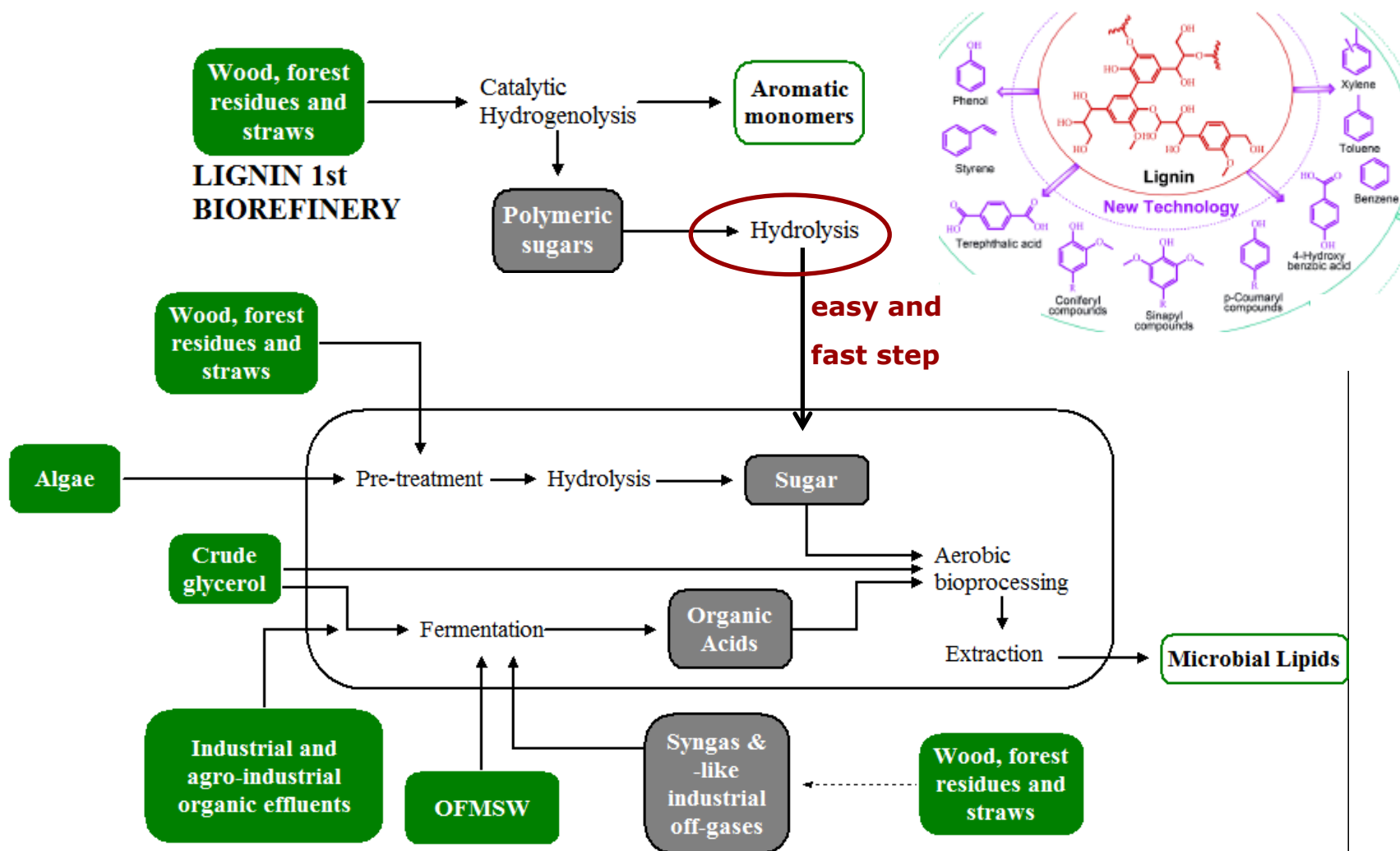
# Microbial lipids from sugars and organic acids

- Technology validated in the lab – what is the challenge for going further?



- Higher volumetric productivities and concentrations; threshold of 90 g/L and 1.3 g/L/h given a yield of 0.28 g lipids / g sugar (Davis et al. 2013, NREL/TP-5100-60223)
- More efficient extraction methods
- Produce high value products along with lipids

# Microbial lipids as part of Lignin-1st biorefinery



# Microbial lipids from sugars and organic acids

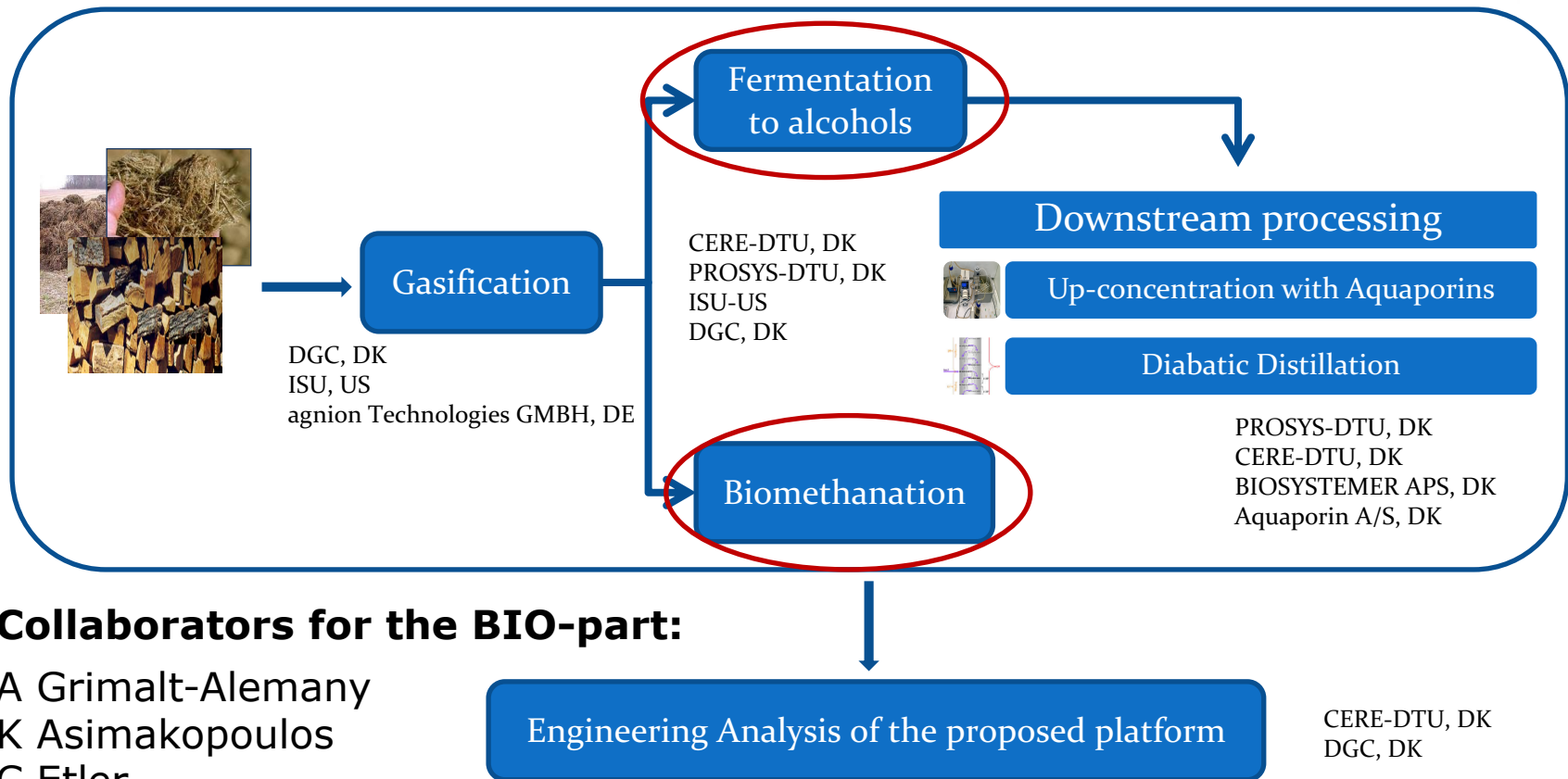
- Reactor development for higher productivities and concentrations
  - Under development for other intracellularly accumulated compounds at DTU- Chem. Eng.
  - Time horizon for lipids at TRL 4 after resources are raised: 3-4 years
  
- Novel solvents and solvent combinations for more efficient extraction based on computer-aided solvent design methods (ICAS software in DTU Chem Eng)
  - Time horizon for TRL 4 after resources are raised: 3-4 years
  
- Lignin 1st biorefinery for obtaining high value products along with lipids
  - Catalytic part is at TRL 3 - 4\*
  - Time horizon for TRL 5 after resources are raised: 3 years

**\*S. Ghafarnejad**, 2018 Catalytic Hydroliquefaction of lignin to Value-Added Chemicals

PhD thesis, DTU-Chemical Engineering, Principal Supervisor: **Anker Degn Jensen**

# Coupling gasification and biochemical conversions

## in the frame of SYNFERON project



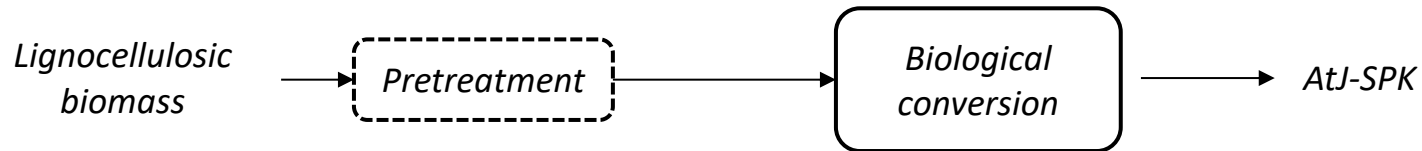
### Collaborators for the BIO-part:

A Grimalt-Aleman  
K Asimakopoulos  
C Etler  
IV Skiadas

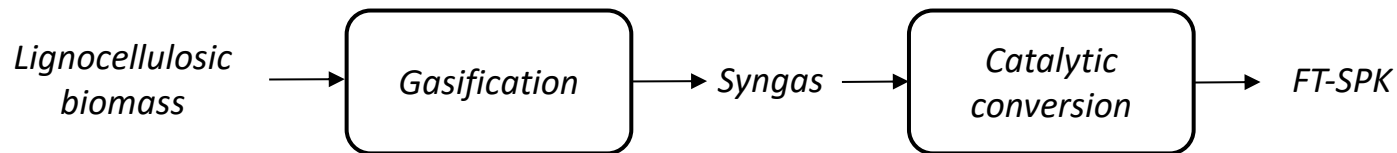
<http://www.cere.dtu.dk/research-and-projects/framework-research-projects/biorefinery-conversions/optimised-syngas-fermentation-for-biofuels-production-synferon>

# Coupling gasification and biochemical conversions for AtJ pathway

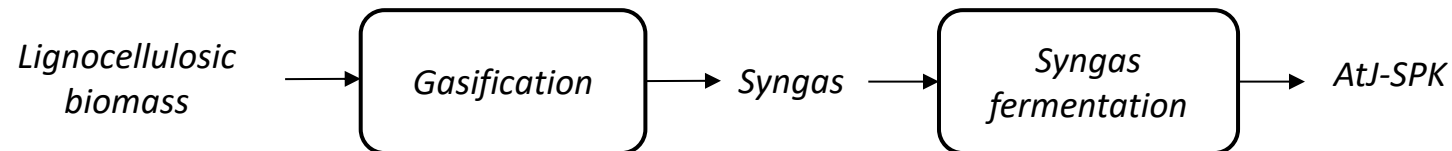
## Biochemical route



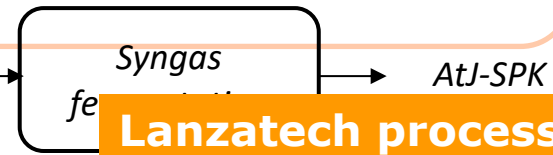
## Thermochemical route



## Thermochemical + Biochemical -> Syngas fermentation



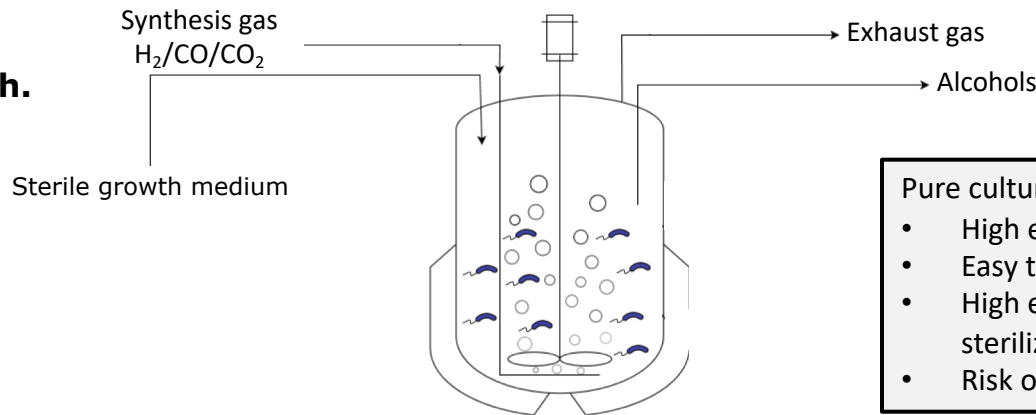
Syngas  
Steel industry



**Lanzatech process**  
**ASTM 2018**

# One step forward for cost reduction at DTU-Chemical Engineering

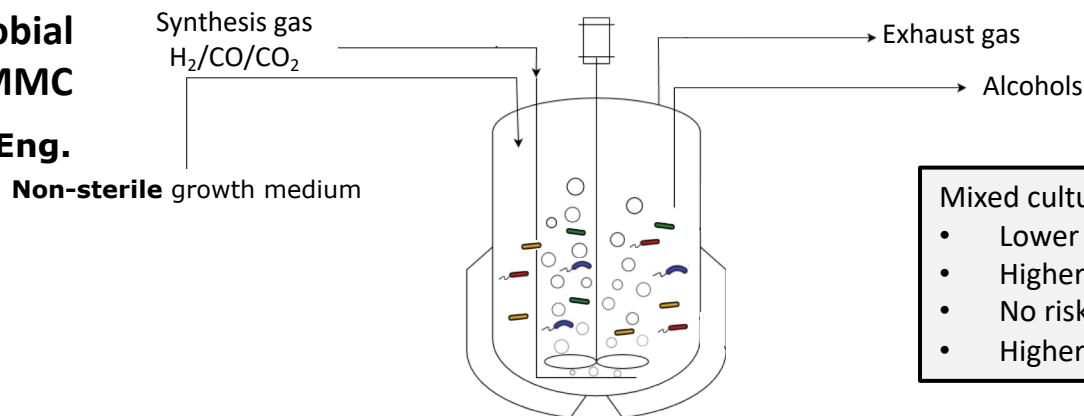
## Pure cultures Lanzatech tech.



### Pure cultures

- High efficiency
- Easy to control
- High energy demand due to sterilization
- Risk of contamination

## Mixed Microbial Consortia, MMC DTU Chem. Eng.



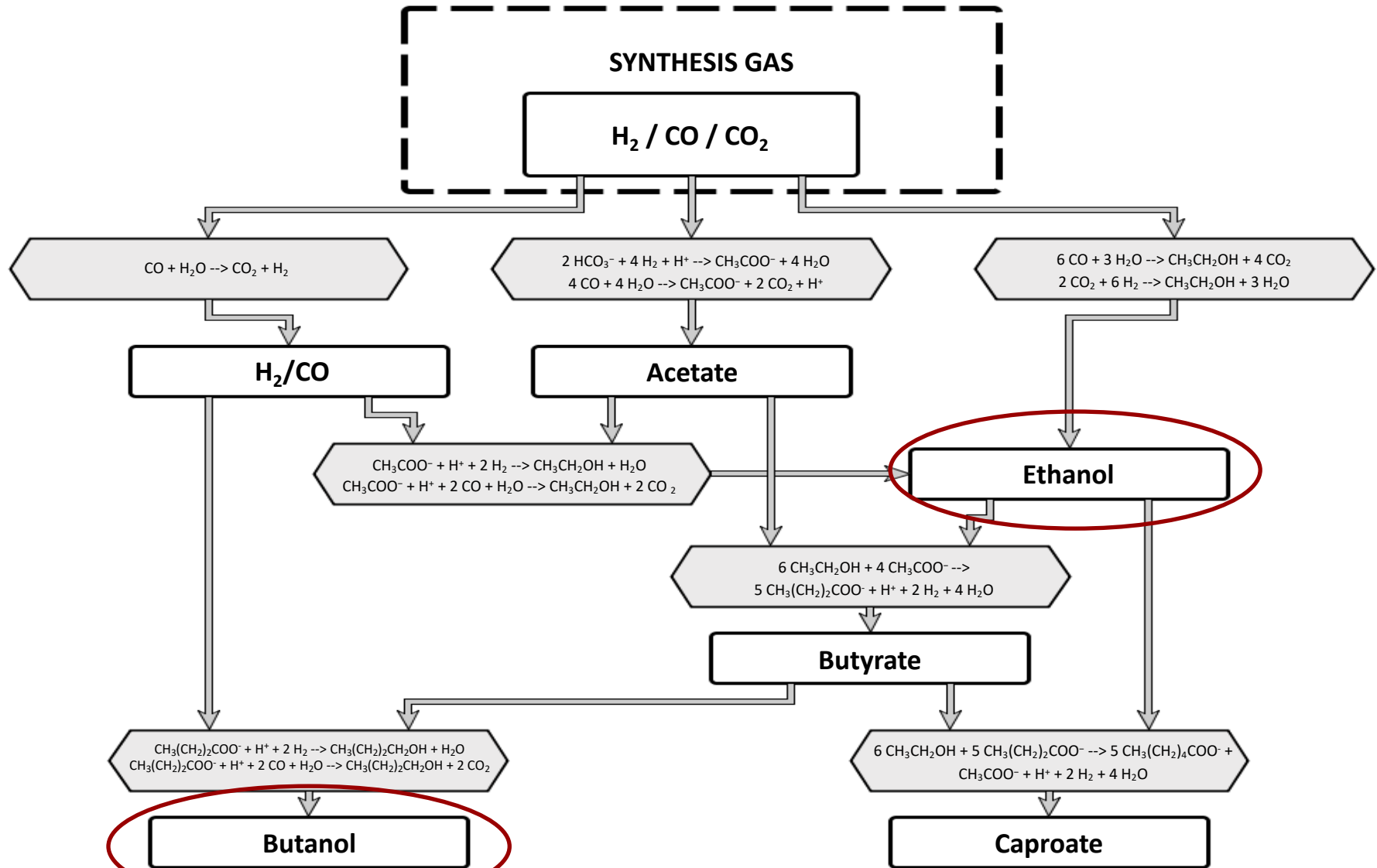
### Mixed cultures

- Lower operational cost
- Higher tolerance and adaptability
- No risk of contamination
- Higher complexity

<http://www.cere.dtu.dk/Research-and-Projects/PhD-Projects/Fermentation-of-Synthesis-Gas-to-gaseous-and-liquid-fuels>

# Syngas fermentation to alcohols

## Metabolic network of acetogenic Mixed Microbial Consortia





# Thermodynamics of net metabolic reactions for metabolic network selectivity towards alcohols

Feasibility study based on  $\Delta_r G'_T$  of all reactions occurring in MMC

## Gibbs free energy change

- $\Delta_r G' = \Delta_r G^\circ(I = 0.08 \text{ M}) + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$
- $\Delta_r G'_T = \Delta_r G'_{298.15 \text{ K}} \cdot \frac{T}{298.15 \text{ K}} + \Delta_r H'_{298.15 \text{ K}} \cdot \frac{298.15 \text{ K} - T}{298.15 \text{ K}}$

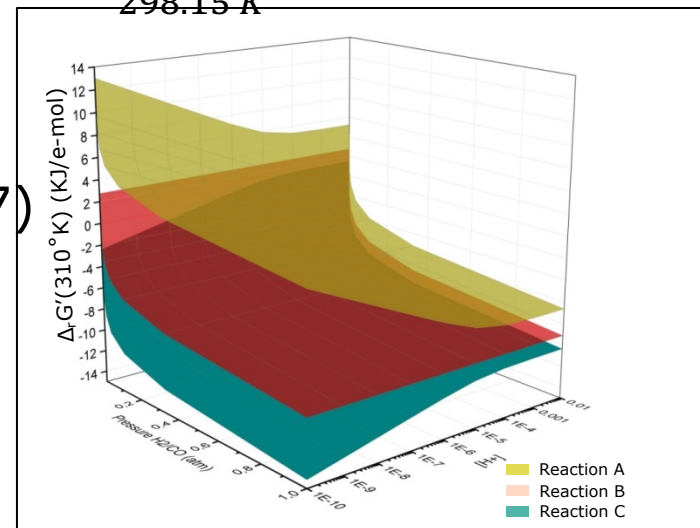
## Thermodynamic potential factor ( $F_T$ )

$$\bullet r = \frac{k_{max} \cdot S}{k_s + S} \cdot X \cdot F_T \quad (\text{Jin \& Bethke 2007})$$

$$\bullet F_T = 1 - \exp\left(-\frac{\Delta G_A - \Delta G_C}{\chi RT}\right)$$

$$\Delta G_A = -\Delta_r G_T$$

$$\Delta G_C = Y_{ATP} \cdot \Delta G_p$$



- $F_T \approx 1$  → Kinetic control  
 $0 > F_T > 1$  → Thermodynamic control  
 $F_T = < 0$  → Metabolism stops

**Grimalt-Alemany et al., 2018 Biotechnology for Biofuels, 11:198,**  
<https://doi.org/10.1186/s13068-018-1189-6>

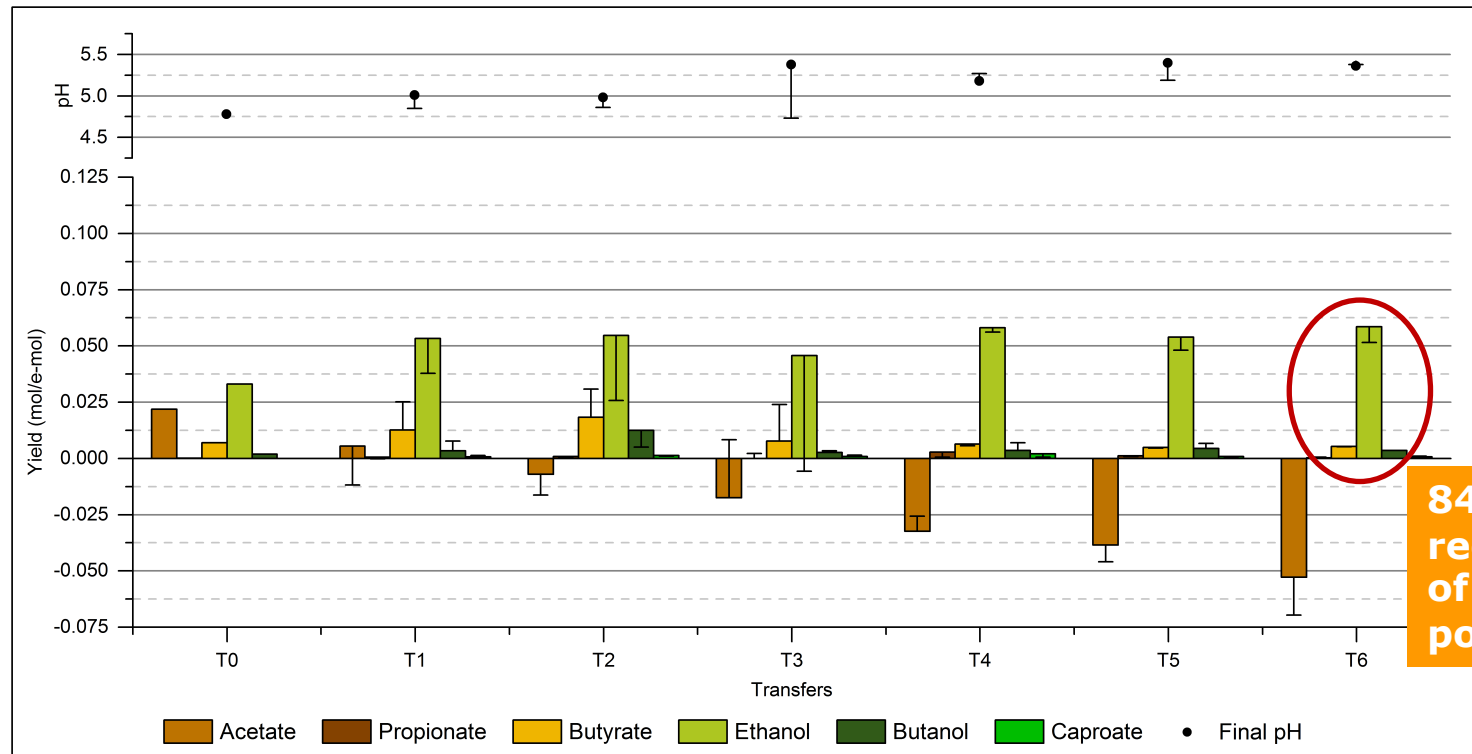
# Syngas fermentation to ethanol

Effect of acetic acid concentration on  $\Delta_r G'_{310K}$  and  $F_T$

Initial conditions:

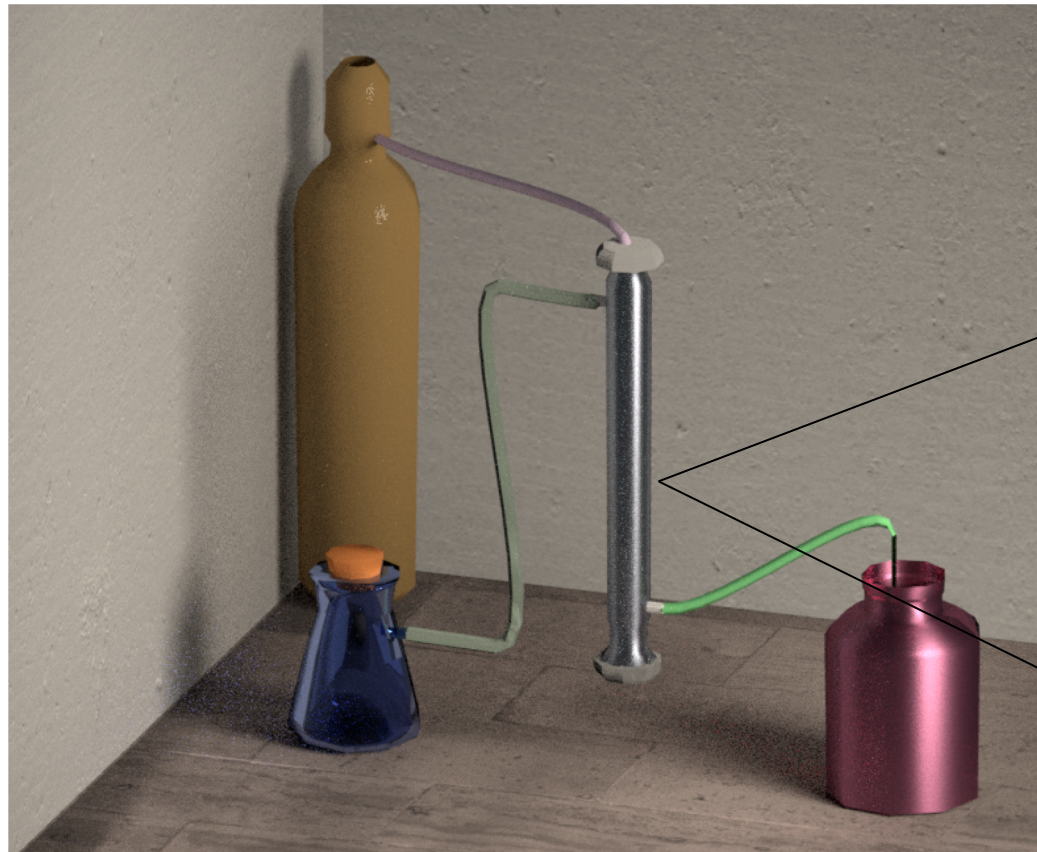
Substrate	-> H <sub>2</sub> (1.05 atm), CO <sub>2</sub> (0.60 atm), CO (0.45 atm)
Product concentration	-> 1 mM except acetate
Temperature	-> 310 K
Ionic strength	-> 0.08 M
pH	-> 5

Product yields (mol/e-mol) - Enriched culture with addition of 20 mM of acetic acid



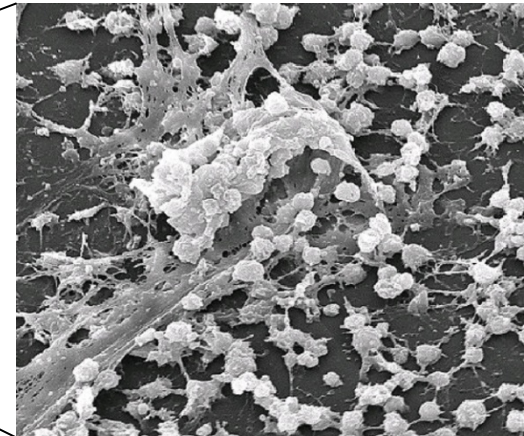
# Tackling mass transfer limitations at DTU-Chem Eng

## Mixed cultures allow for biofilm-based processes



### ➤ Trickle bed reactor

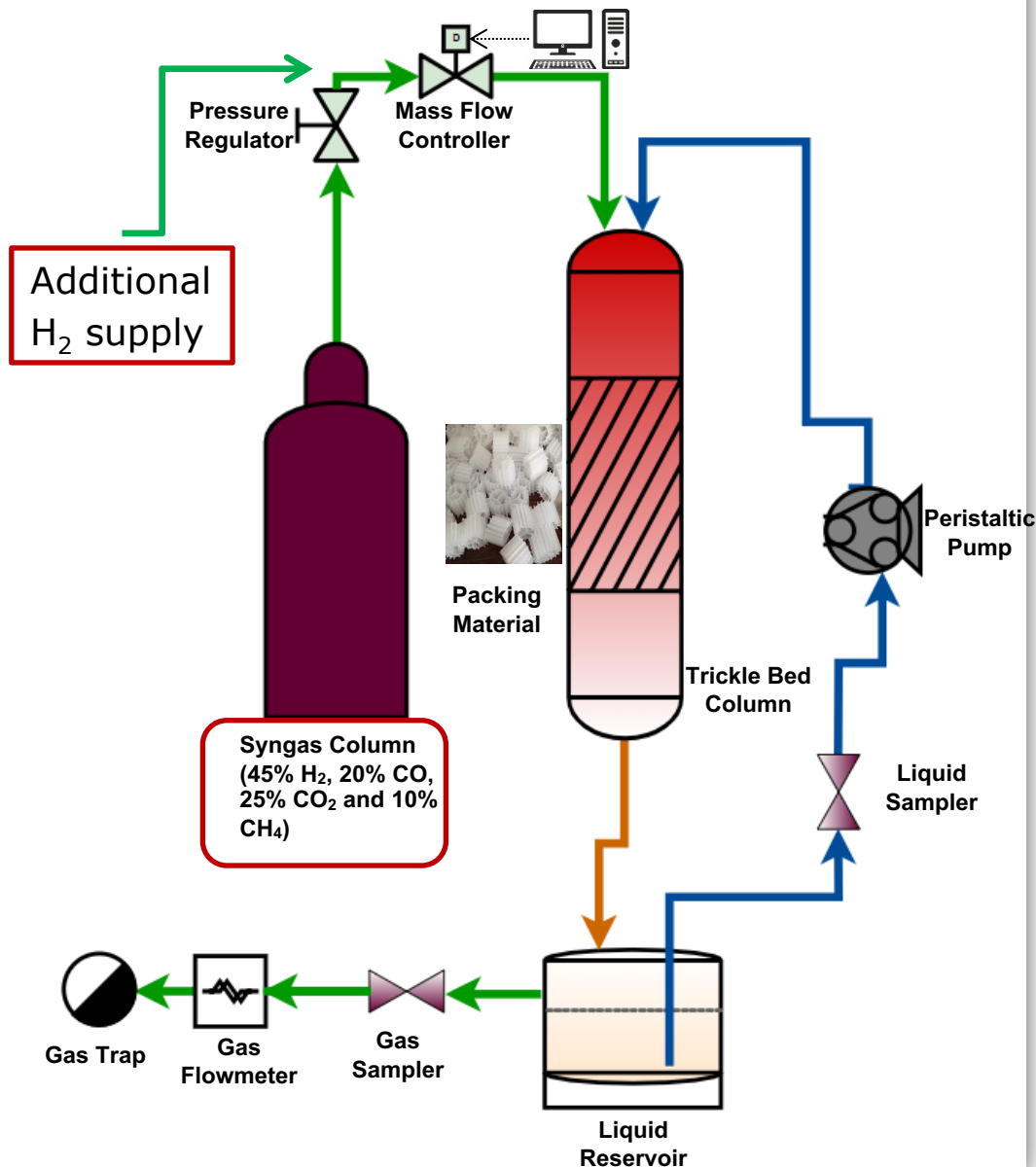
- High Mass Transfer Rates
- Biofilm formation



<http://www.cere.dtu.dk/Research-and-Projects/PhD-Projects/Fermentation-of-Synthesis-Gas-and-design-of-bioreactors>

# Trickle Bed Reactor – operating conditions

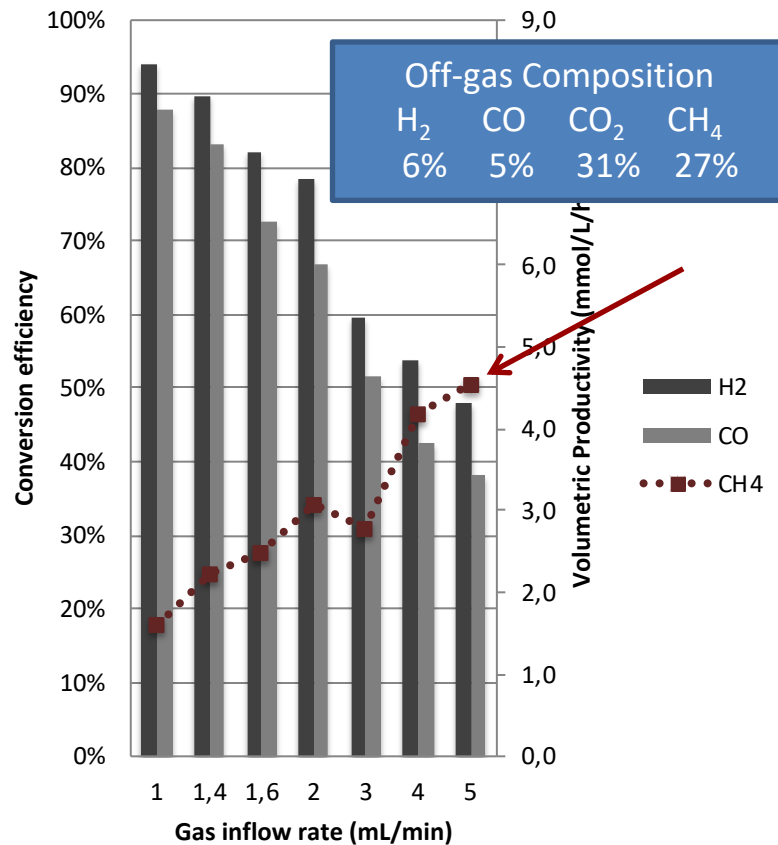
- So far tested for syngas-to-CH<sub>4</sub> with and without additional H<sub>2</sub> supply
- Temperature: 37 and 60 °C
- # pH control
- Pressure: 1 atm



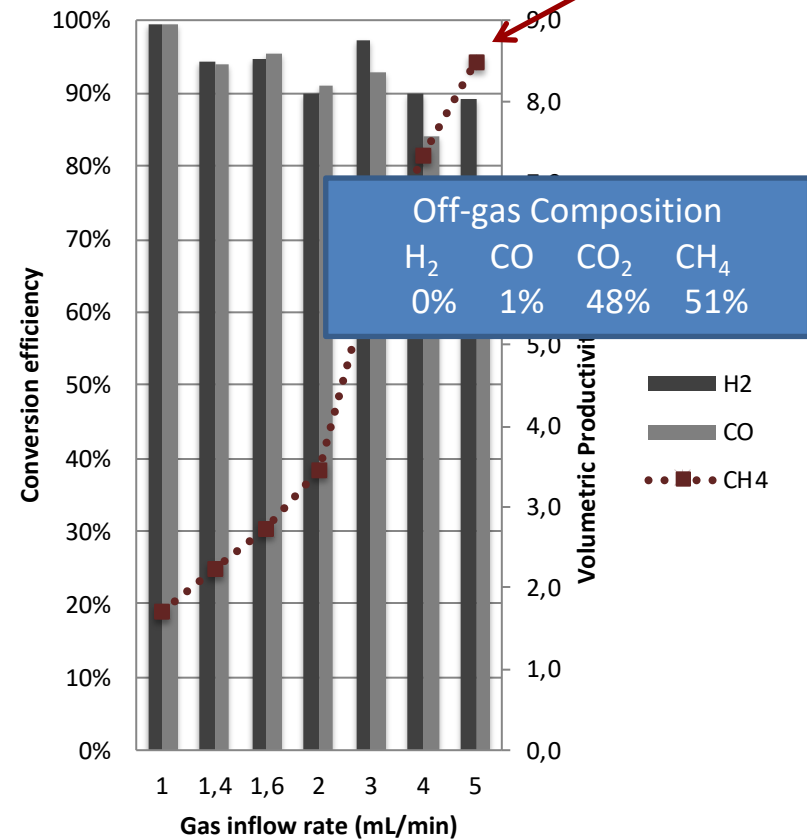
# Conversions and production rates

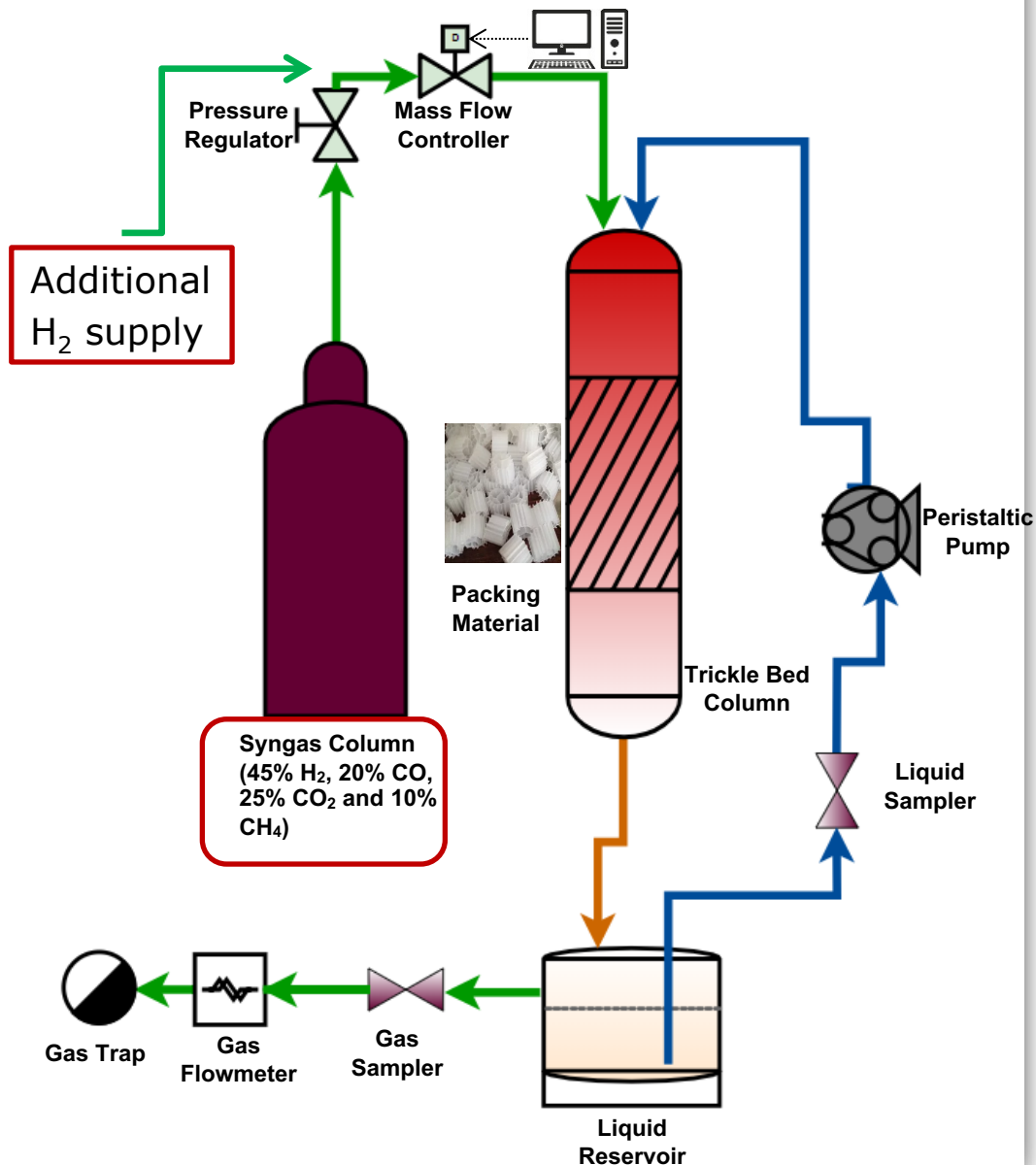
! >100% enhancement compared to best reported production rates

## Mesophilic



## Thermophilic





## Trickle Bed Reactor – with additional H<sub>2</sub>

- Conversion efficiency

H <sub>2</sub>	CO	CO <sub>2</sub>
99.5%	99.5%	97.8%

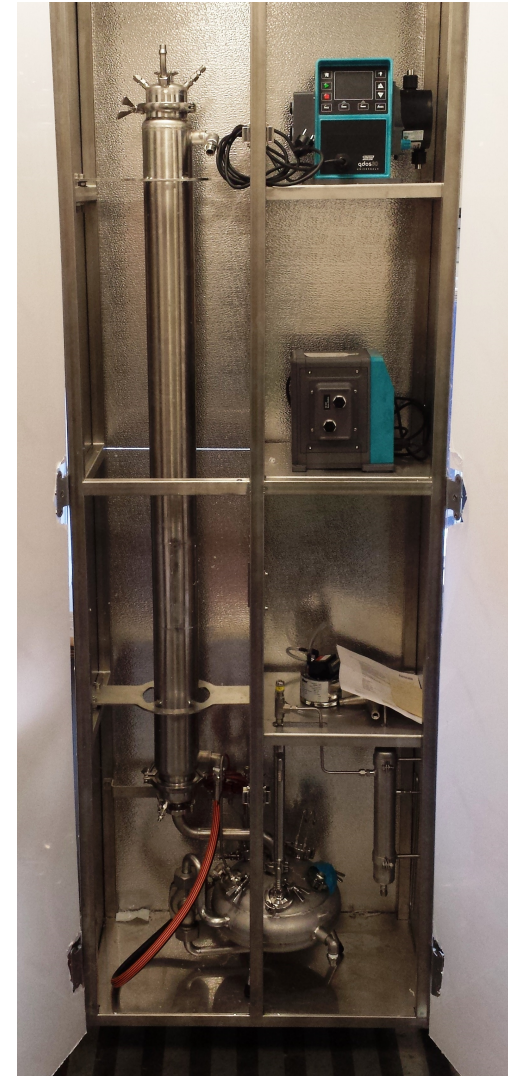
- Off-gas composition

H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>
2%	0%	2%	96%

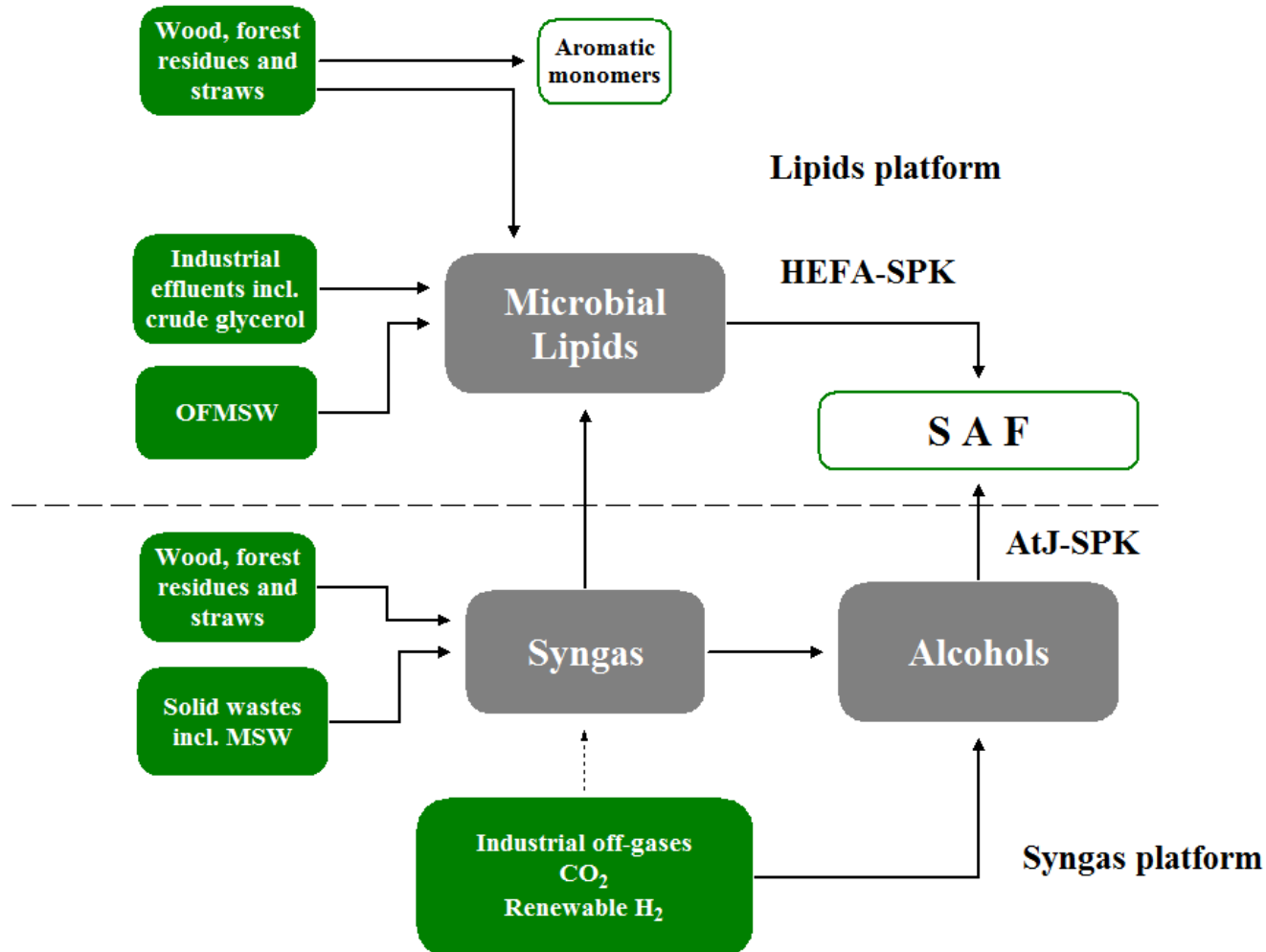


# Status of syngas bio-transformations in the trickle-bed reactor

- Currently being tested for alcohols production at lab-scale
- Up-scaling and construction finished
- High conversion efficiency of syngas and upgrading with  $H_2$  to be validated at pilot-scale
- Status in 2019:
  - Syngas-to- $CH_4$  and gas upgrading: TRL 5
  - Syngas-to-alcohols: TRL 3 and time horizon for TRL 5 if resources are raised: 2 years
  - Syngas to lipids: follows microbial lipids planning: 3-4 years for TRL 5



# Our vision on Advancing Bio-manufacturing for SAF in combination with thermochemical/catalytic/renewable electricity routes





# From proof-of-concept to demonstration: Pilot-facilities at DTU - Chemical Engineering

- 700 m<sup>2</sup> pilot plants, laboratories and workshop + 500 m<sup>2</sup> under construction



# Column operations



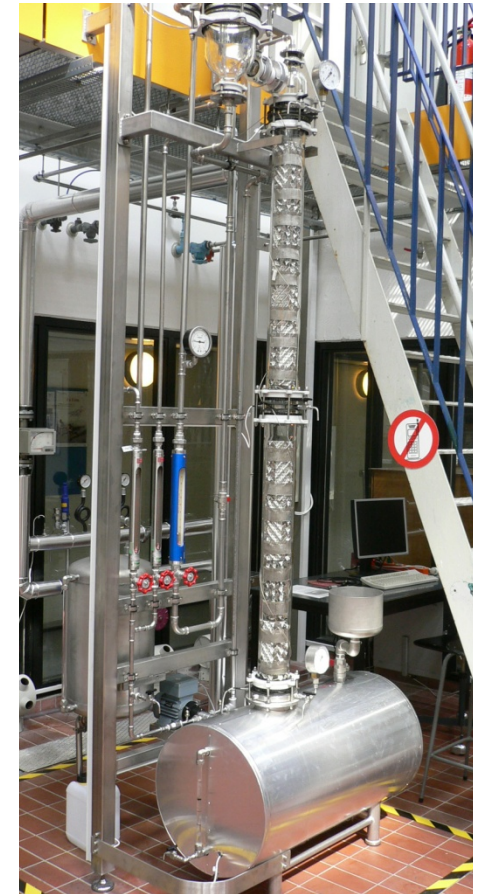
Continuous distillation  
in bubble-cap tray column



Absorption of ammonia in  
packed column



Batch distillation  
of alcohols  
using structured  
packing



Hydrodynamics of gas/liquid flow in packed columns



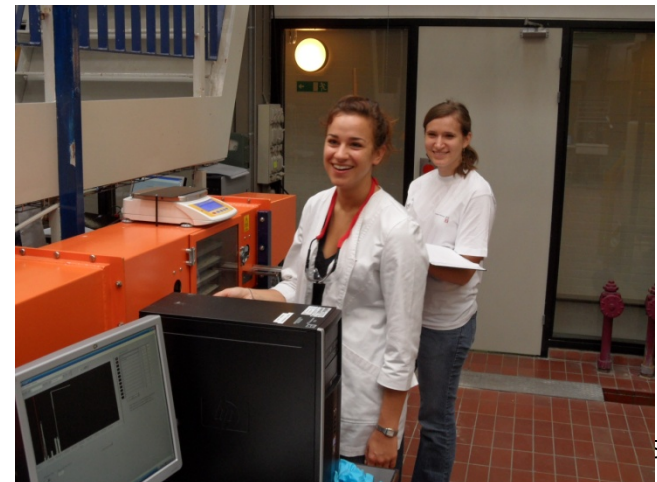
# Drying processes



Fluidization and fluid bed drying



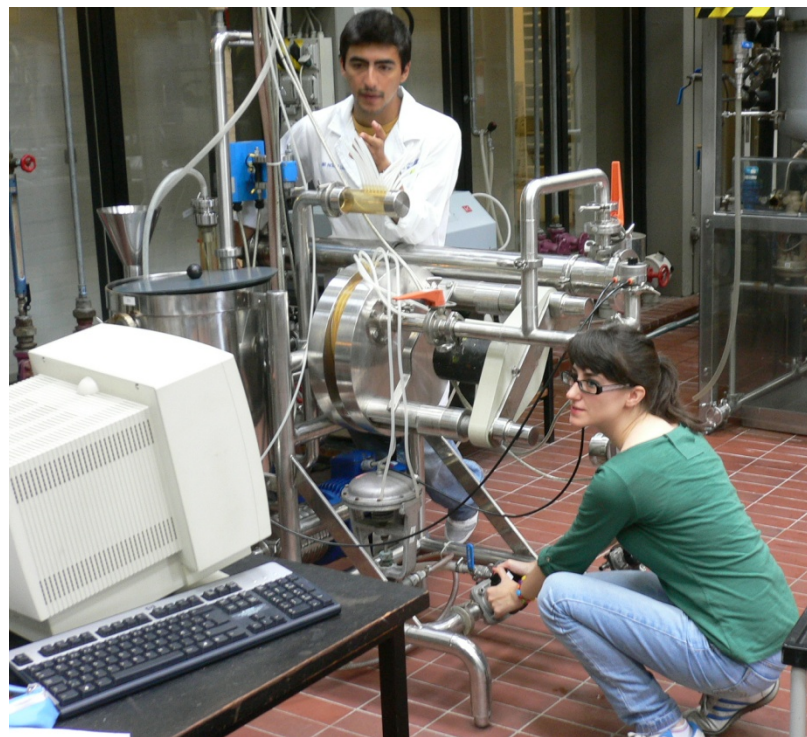
Spray drying



Drying on trays  
in a tunnel

# Separation processes, 1

Disk-stack centrifugation



Ultrafiltration





# Separation processes 2

Vacuum crystallisation

Ammonia  
tray stripper

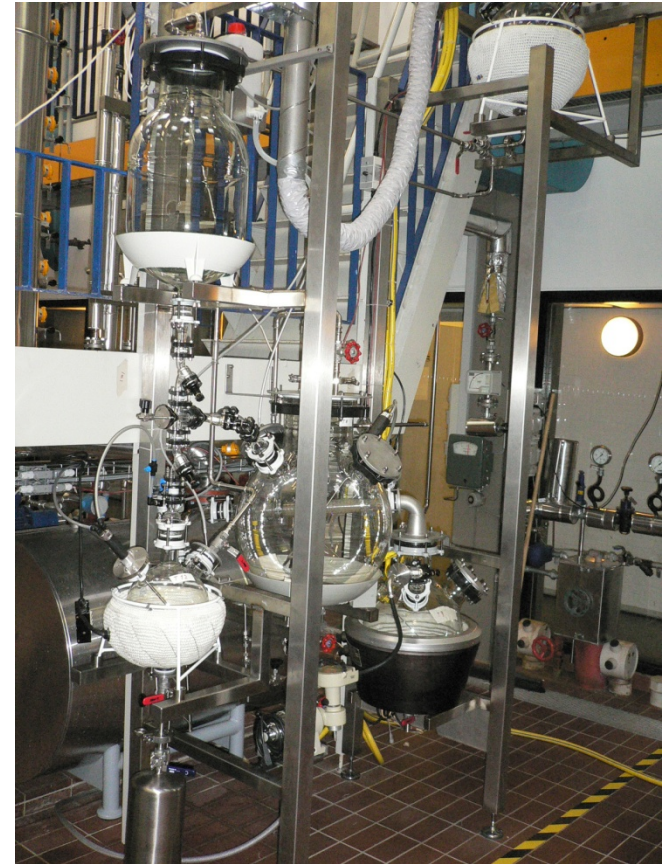


Evaporation in falling film evaporator

# Chemical and biochemical reactions



Fixed bed for immobilized enzyme processes, ion exchange or chromatographic separations



Multipurpose plant for organic synthesis



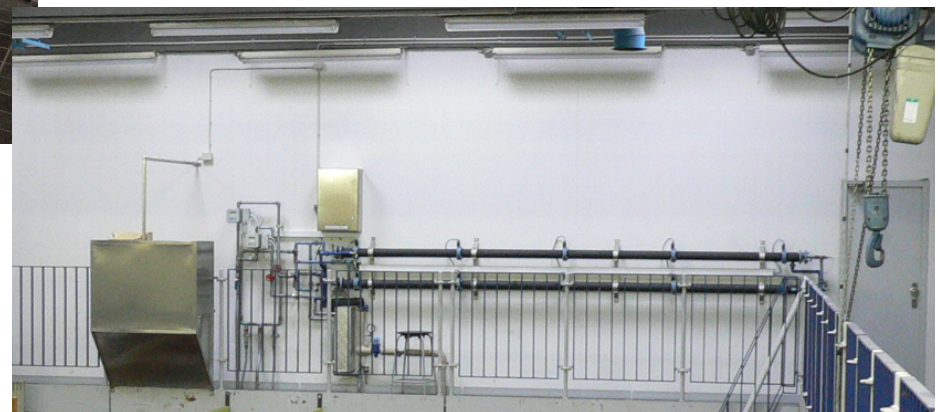
# Other operations



Liquid/liquid extraction



Solid/liquid extraction



Heat transfer in pipes and plate heat exchangers

# Fermentation



An advanced fermentation platform with lab- and pilot- fermentors will be established in DTU Chemical and Biochemical Engineering Dept. within 2019



THANK YOU !