

Thermochemical conversion of biomass

Liquid Fuels

François Maréchal

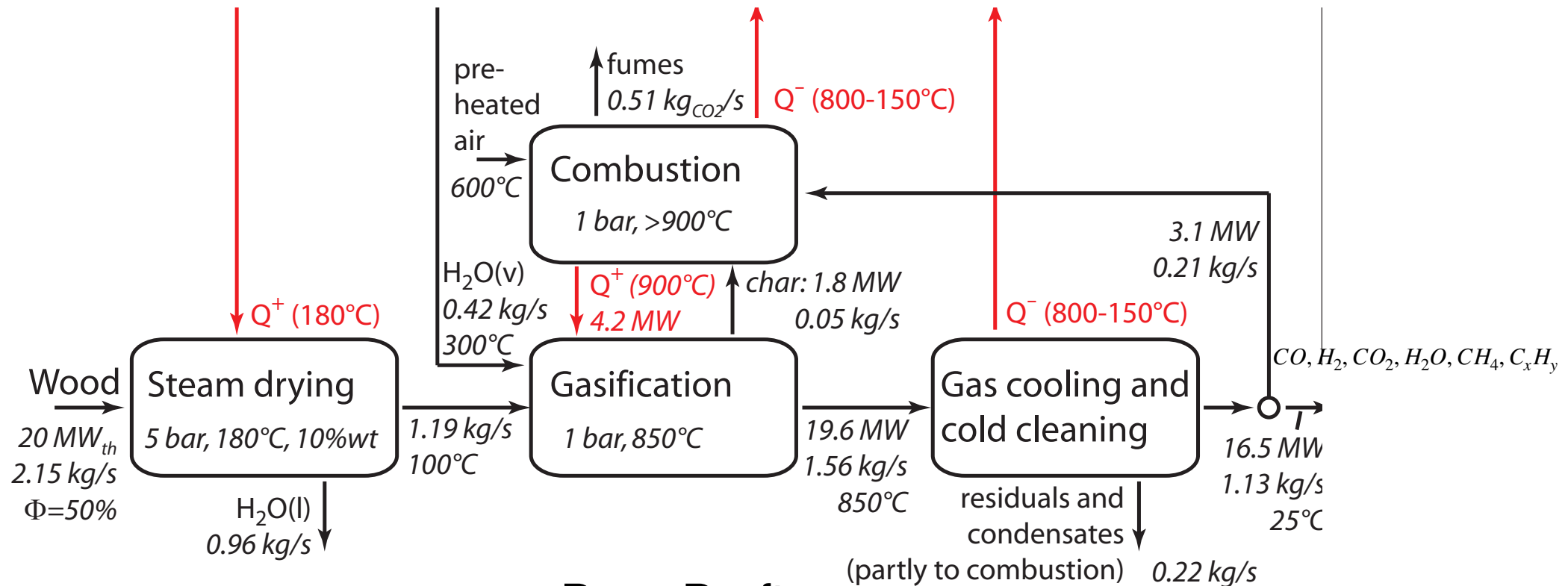
IPESE

Industrial Process and Energy Systems Engineering

EPFL Valais-Wallis

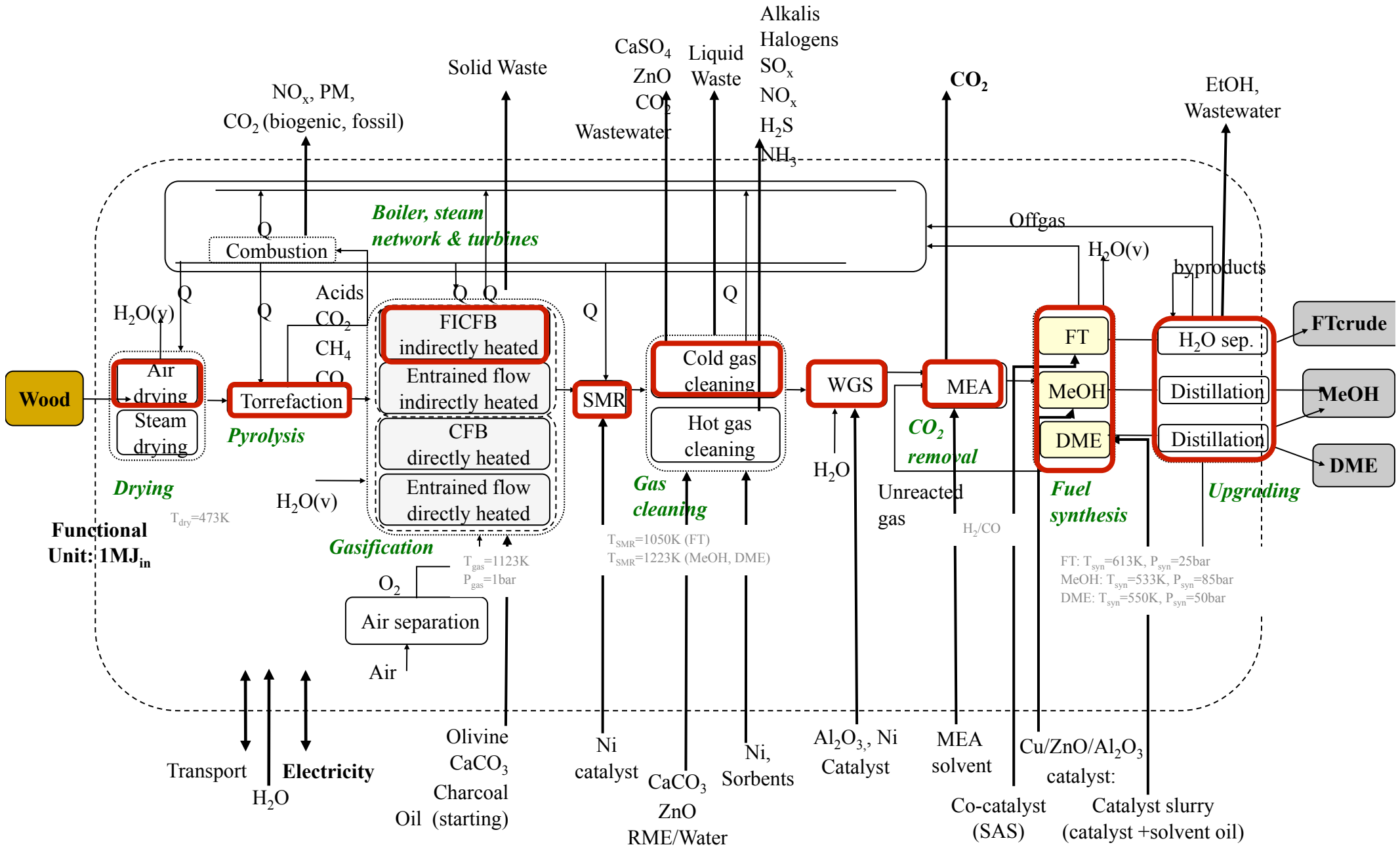
CH - 1950 Sion

SOLID -> SYNGAS



DownDraft
Entrained flow
Indirectly heated
Multi-stage

Process Superstructure



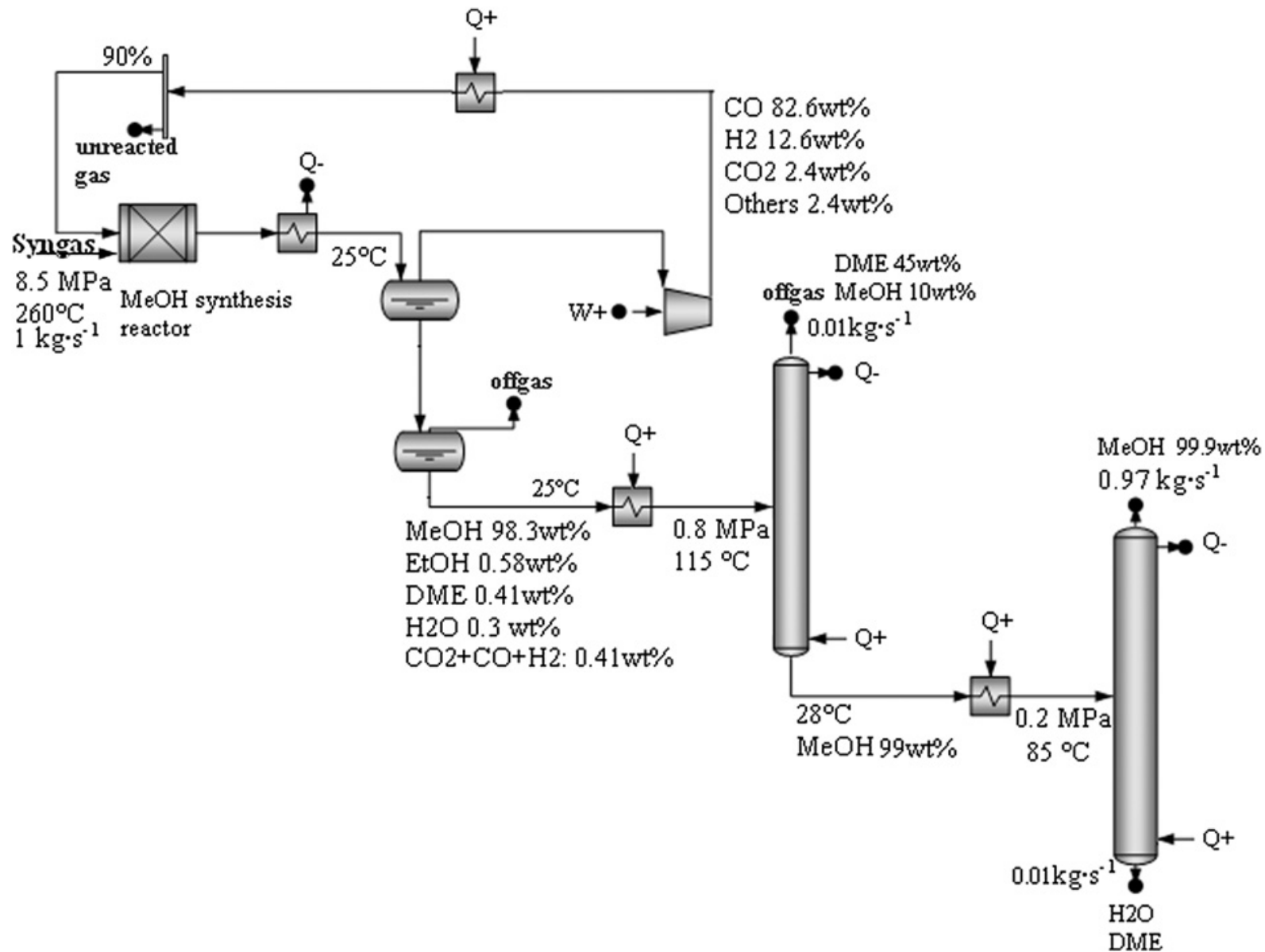
⁴Gassner, M. & Maréchal, F., Thermo-economic process model for the thermochemical production of Synthetic Natural Gas (SNG) from lignocellulosic biomass. *Biomass & Bioenergy*, 33(11):1587–1604, 2009. ⁵Tock, L., Gassner, M. & Maréchal, F., Thermo-economic process model for thermochemical production of liquid fuels from lignocellulosic biomass, submitted to Biomass & Bioenergy 2009.

FT- MEOH - DME reactions

Table 1 – Chemical reactions occurring in the process.

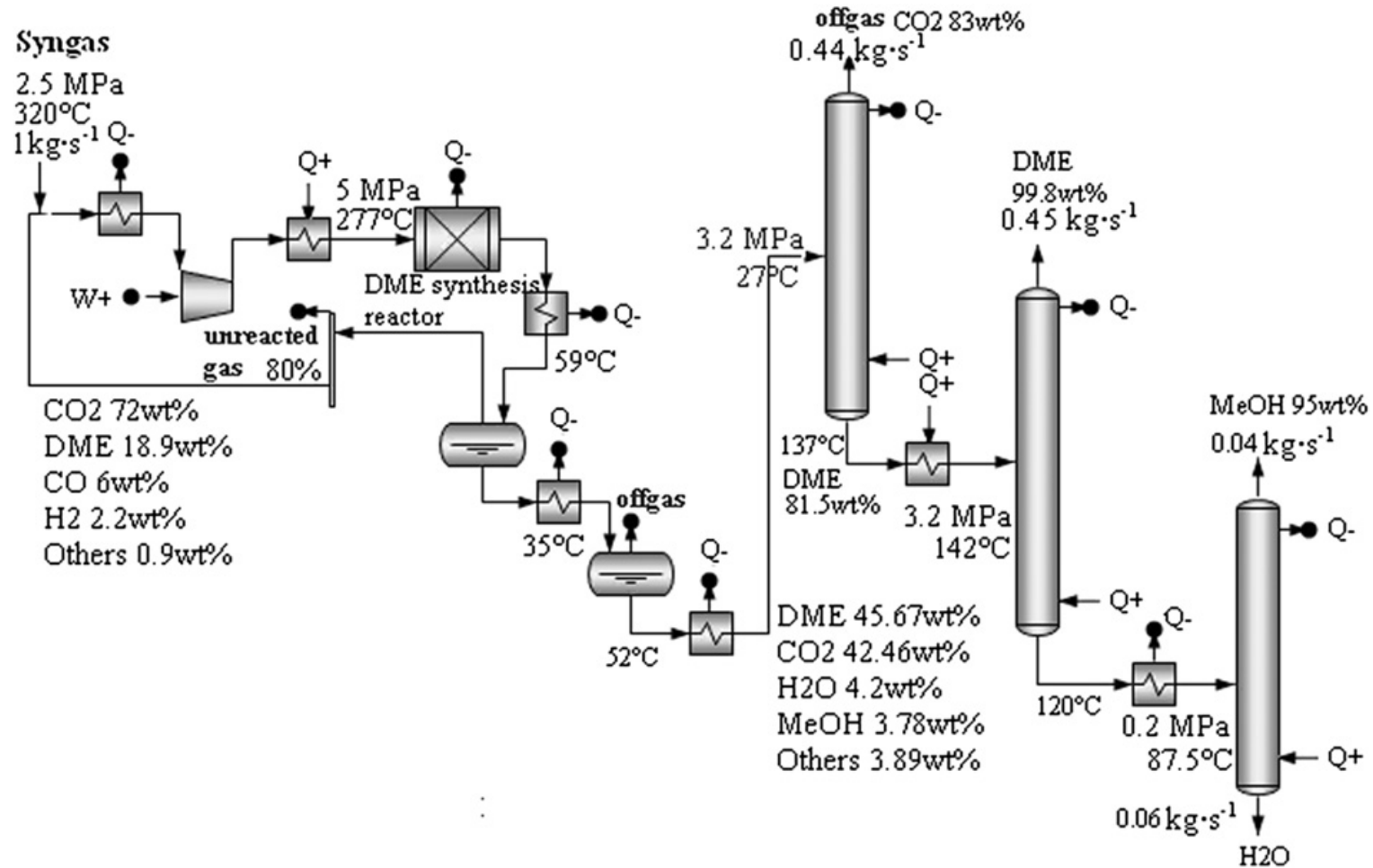
Name	Reaction	$\Delta \hat{h}_r^0 [\text{kJ} \cdot \text{mol}^{-1}]$	Reactor
Alcohols formation	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}$ (6)		FT
FT chain growth reaction	$\text{CO} + 2\text{H}_2 \rightarrow -\text{CH}_2 - + \text{H}_2\text{O}$ (7)	-165	FT
Olefins formation	$2n\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$ (8)		FT
Paraffins formation	$(2n+1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$ (9)		FT
Methanol dehydration	$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ (10)	-23.4	DME, MeOH
One-step DME synthesis	$3\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{CO}_2$ (11)	-246	DME
Two step DME synthesis	$2\text{CO} + 4\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ (12)	-205	DME
Methanol synthesis	$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ (13)	-90.8	MeOH, DME
	$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ (14)	-49.2	MeOH
Ethanol formation	$2\text{CH}_3\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ (15)	-71.8	MeOH
Steam methane reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ (16)	206	SMR
Ethene reforming	$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2$ (17)	210	SMR
Water–gas shift equilibrium	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ (18)	-41	SMR, WGS
			DME, MeOH

MEOH production process



Flowsheet of the MeOH synthesis and upgrading for a normalized syngas stream of 1 kg s^{-1} at the inlet.

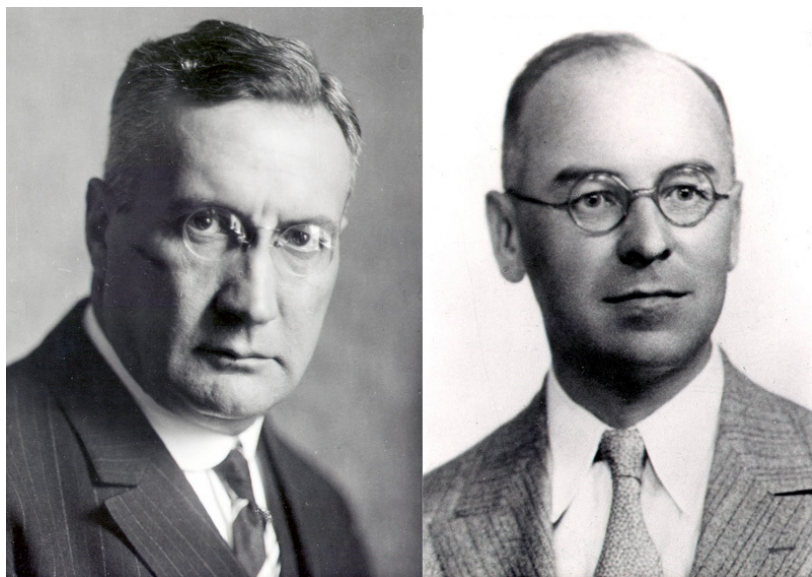
DME production



Flowsheet of the DME synthesis and upgrading for a normalized syngas stream of 1 kg s⁻¹ at the inlet.

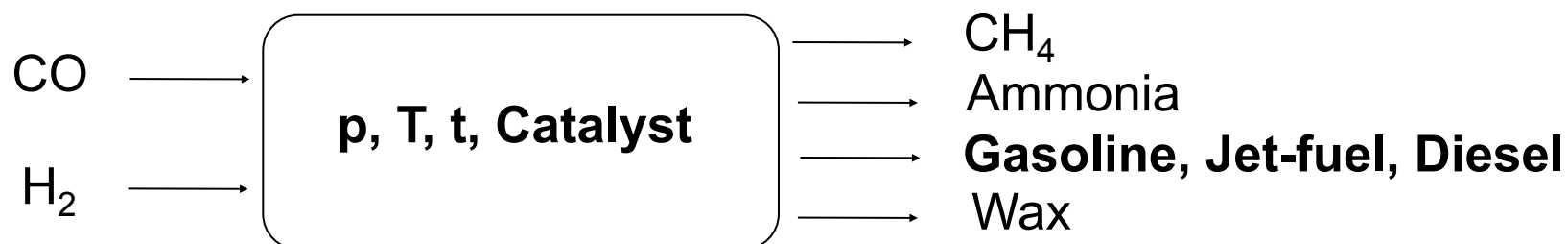
Fischer – Tropsch process

Image: Max Planck Institute of Coal Research.



Franz Fischer and Hans Tropsch developed in Germany in the 1920s

- Historical importance – Fuels from Coal
 - **WWII** – Germany
 - **Apartheid** in South Africa – Sasol
- Drop in Fuel
 - No changes in the infrastructure/fleet



Temperature is controlling the species distribution 7

Process Performance - Comparison

◆ Performance indicators

➤ Overall energy efficiency ϵ_{tot}

- Expressed on the basis of the lower heating value of dry substance

$$\epsilon_{\text{tot}} = \frac{\Delta h_{\text{fuel,out}}^0 \times \dot{m}_{\text{fuel}}^- + \dot{Q}^- + \dot{E}^-}{\Delta h_{\text{biomass,in}}^0 \times \dot{m}_{\text{biomass}}^+ + \dot{Q}^- + \dot{E}^+}$$

➤ Chemical efficiency ϵ_{chem}

- $\dot{E}$ substituted by a natural gas fuel equivalent: NGCC/HP

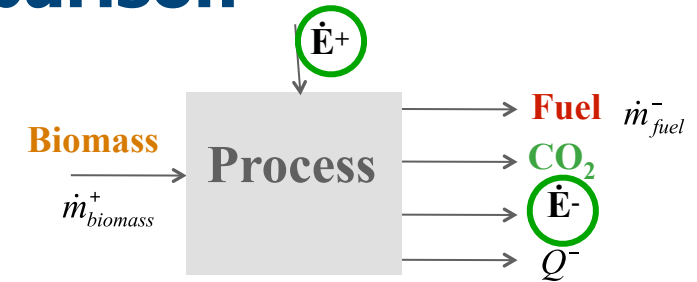
$$\epsilon_{\text{chem}} = \frac{\Delta h_{\text{fuel,out}}^0 \times \dot{m}_{\text{fuel}}^- + \frac{1}{\eta_{\text{NGCC}}} \frac{\Delta h_{\text{SNG}}^0}{\Delta k_{\text{SNG}}^0} \left(\frac{1}{\eta_{\text{HP}}} \dot{Q}^- + \dot{E}^- \right)}{\Delta h_{\text{biomass,in}}^0 \times \dot{m}_{\text{biomass}}^+}$$

$$\eta_{\text{NGCC}} = \eta_{\text{HP}} = 55\%$$

➤ Environmental performance

- Cradle-to-gate LCA approach⁵
- Impact assessment method: Impact 2002+ method
- Functional unit: 1MJ of biomass at the installation inlet

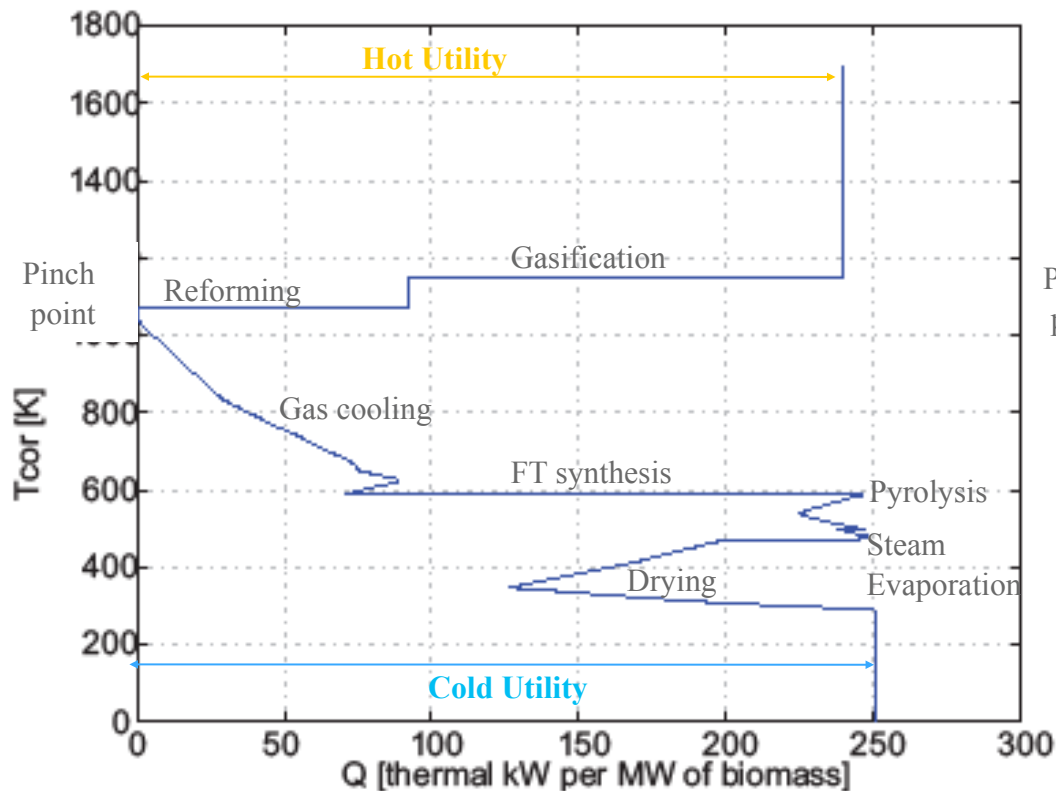
➤ Plant capacity of 20MW_{th} of biomass



⁵Gerber, L., Gassner, M. & Maréchal, F., Integration of LCA in a thermo-economic model for multi-objective optimization of SNG production from woody biomass. In Proceedings of the 19th ESCAPE, Cracow, Poland

FT Process Performance – Energy Integration

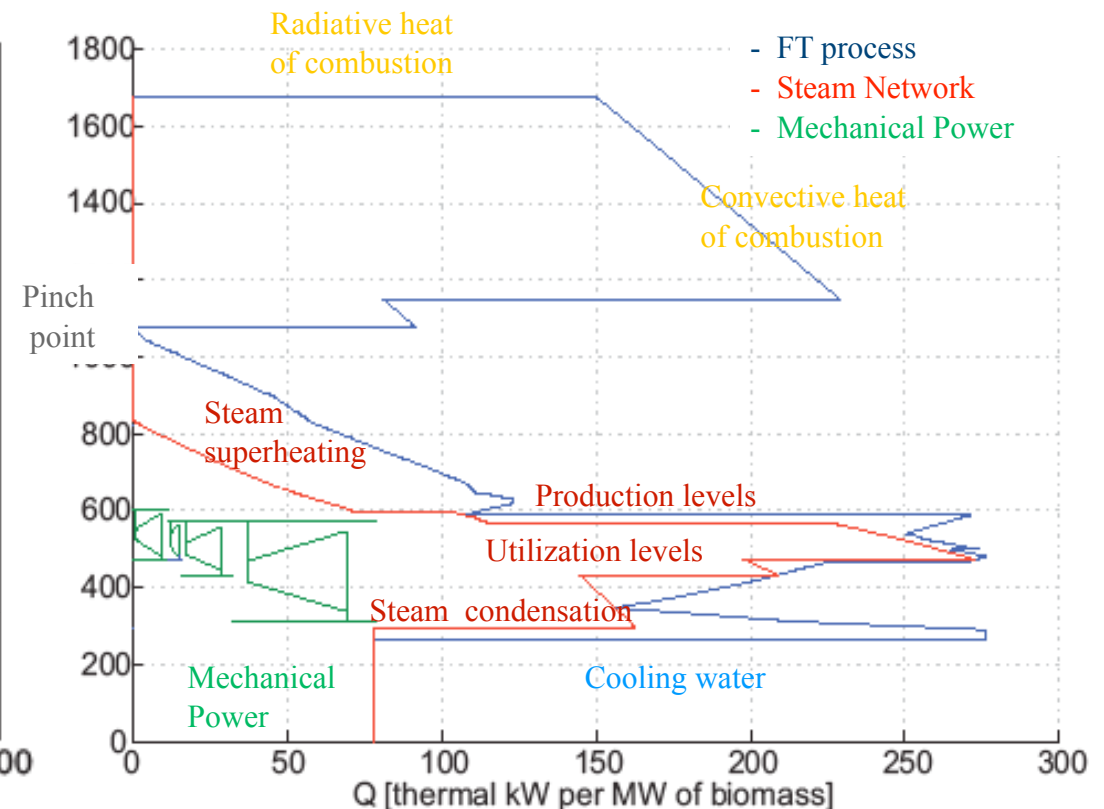
- Maximum heat recovery & heating and cooling requirements for FT process



→ Energy performance

- Valorize heat excess
→ Rankine cycle

- Optimal energy conversion & combined heat and power production for FT process



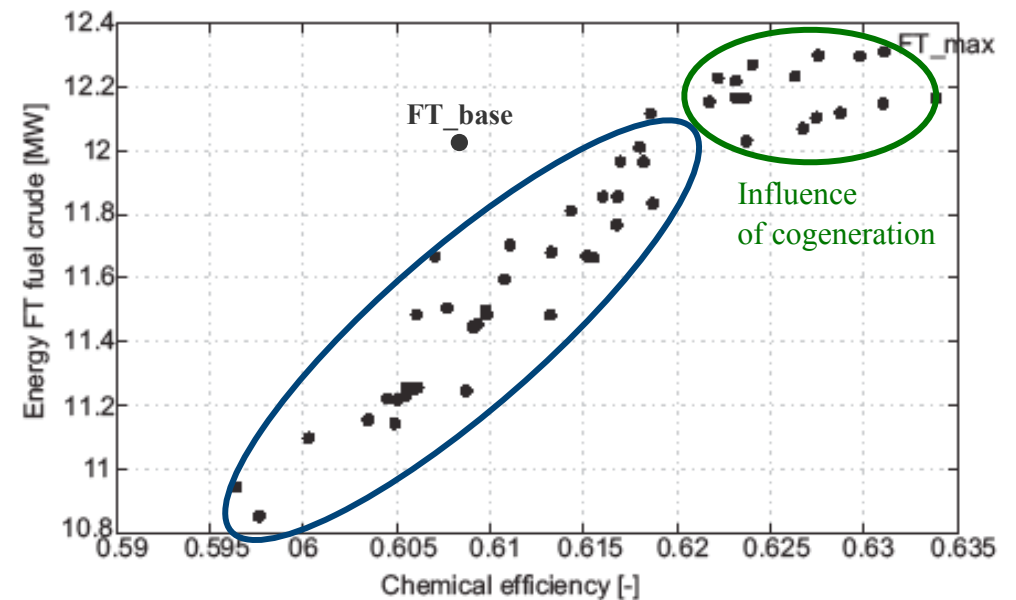
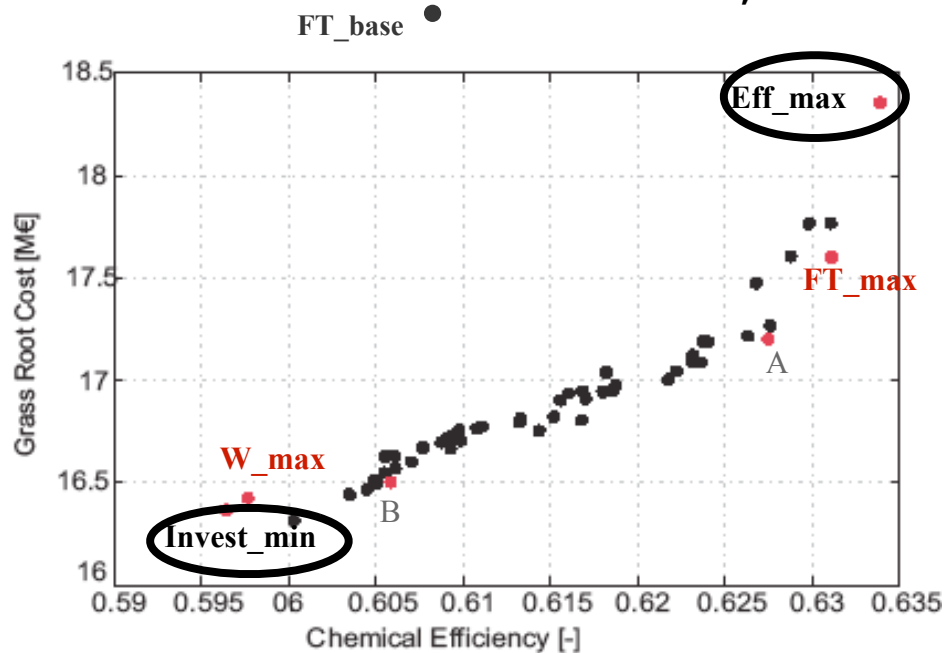
→ Steam network

- 2 production, 2 usage & 1 condensation level
→ Efficiency increase of **17%**

Process Performance - Optimization

- ◆ Multi-objective optimization: Pareto optimal frontier

FT process, 20MW_{th,biomass} indirect fluidized bed gasification

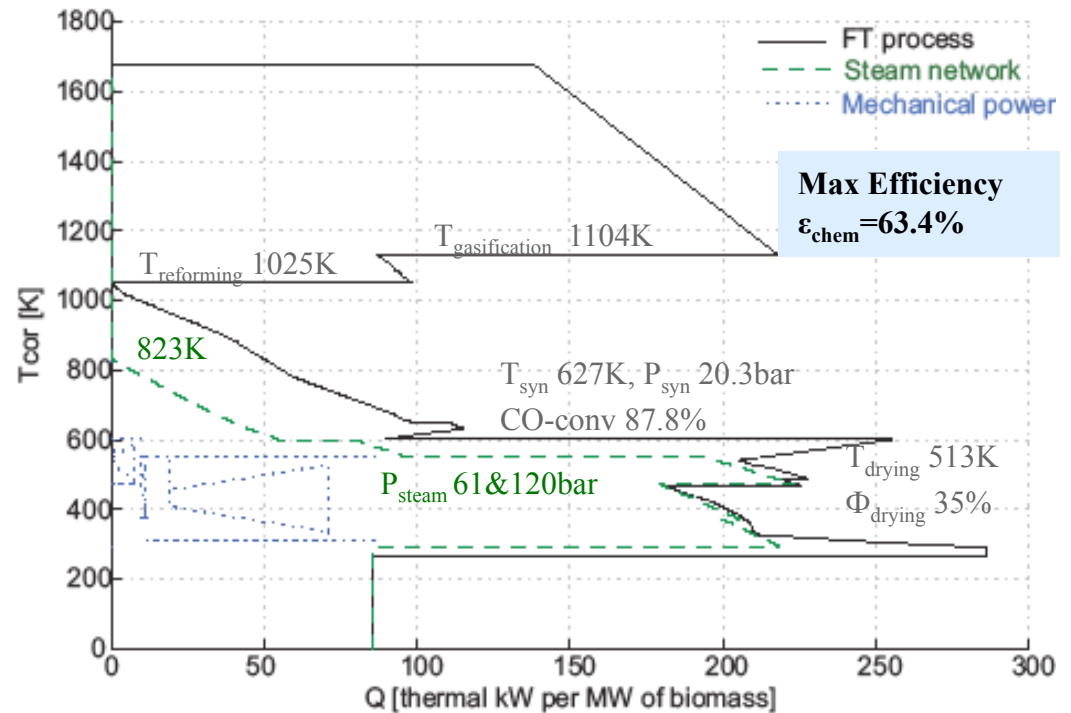
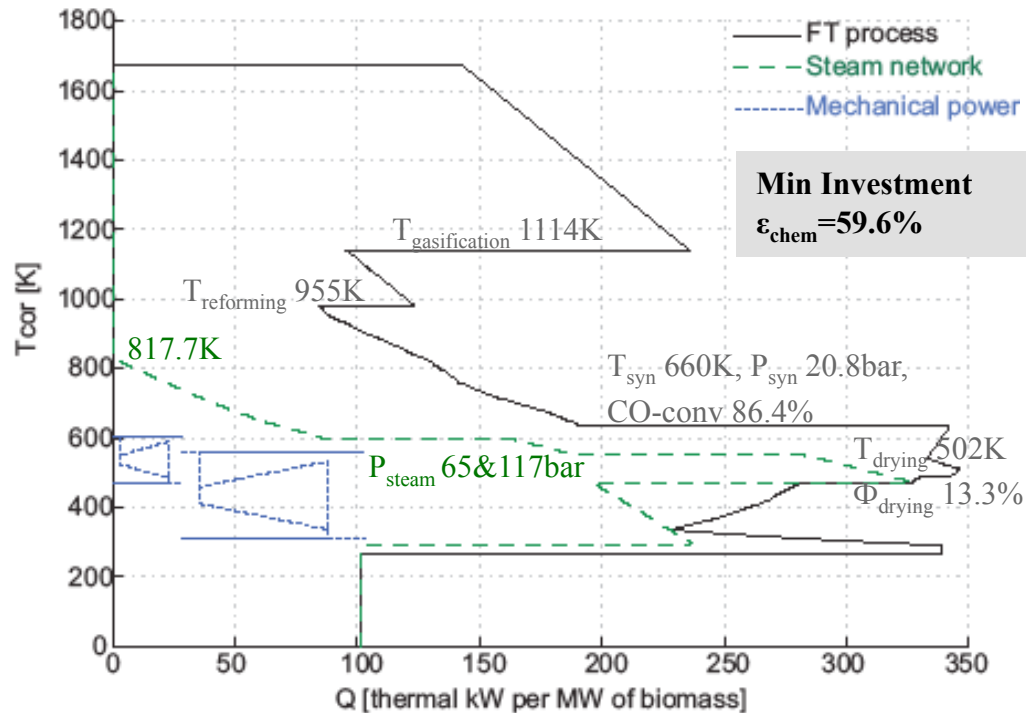


→ Efficiency ↗ Investment ↗
 → Trade-off
 mechanical power & fuel generation

→ Efficiency ↗
 FT-crude fuel ↗
 → Influence of process operating
 conditions on process integration !

Process Performance - Optimization

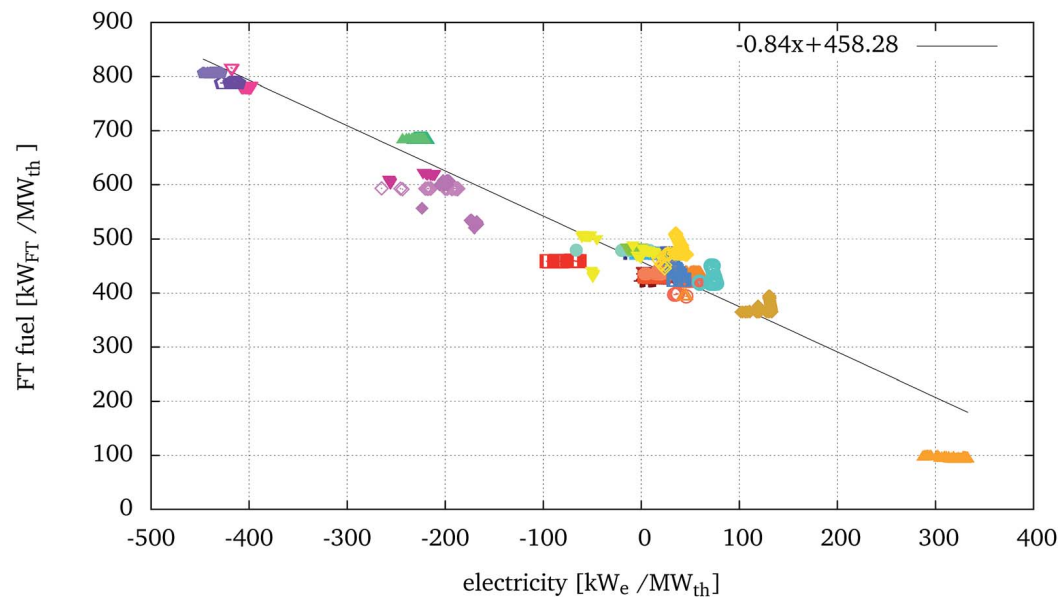
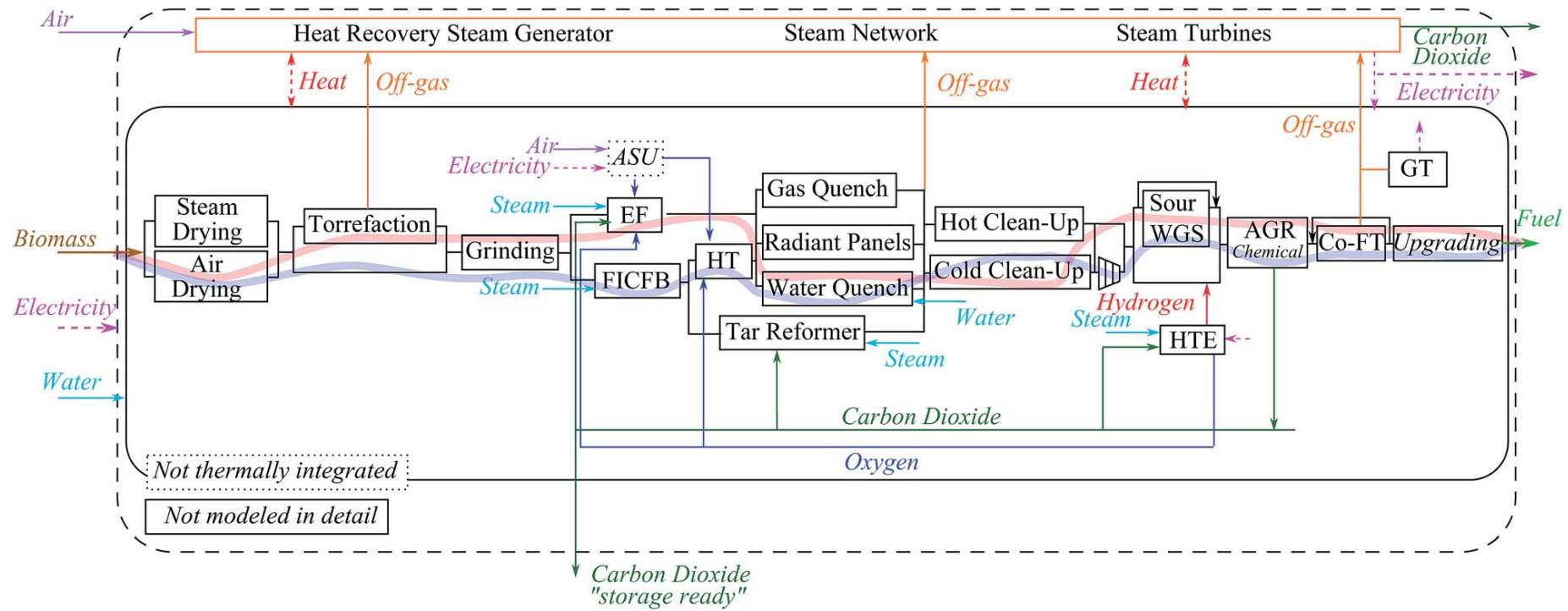
◆ Energy Integration influence on performance



Power balance [kW/MW]	Base case	Min Cost	Max Efficiency
Consumption	85	77	74
Generation	92.5	107	90
Net electricity	7.5	30	16

➔ *Steam network well integrated
Large amount of excess heat recovered*

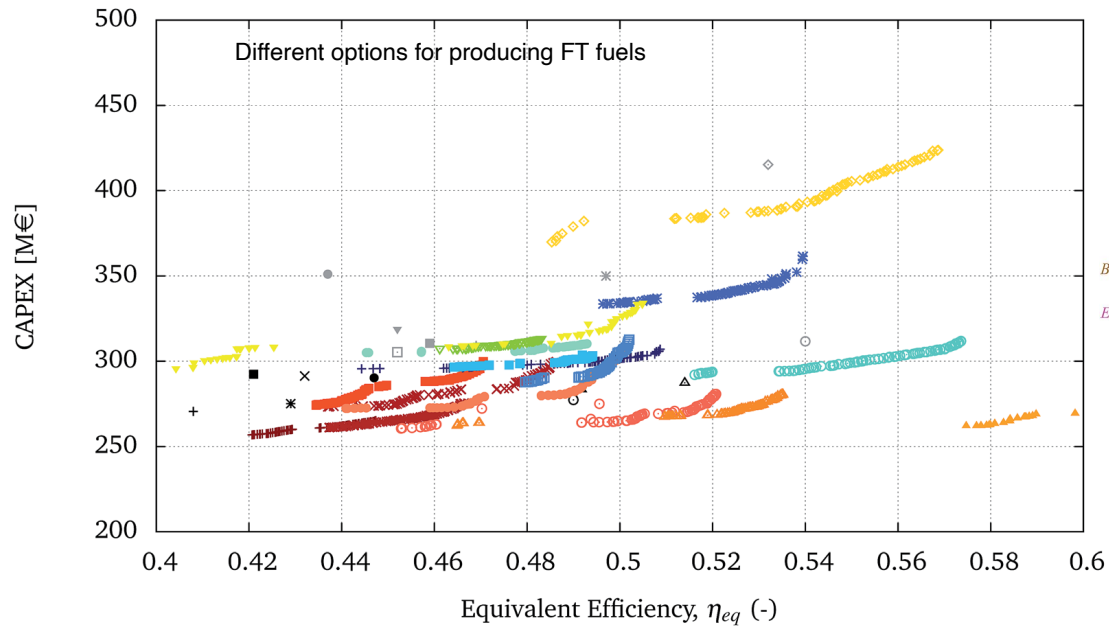
Different process configuration



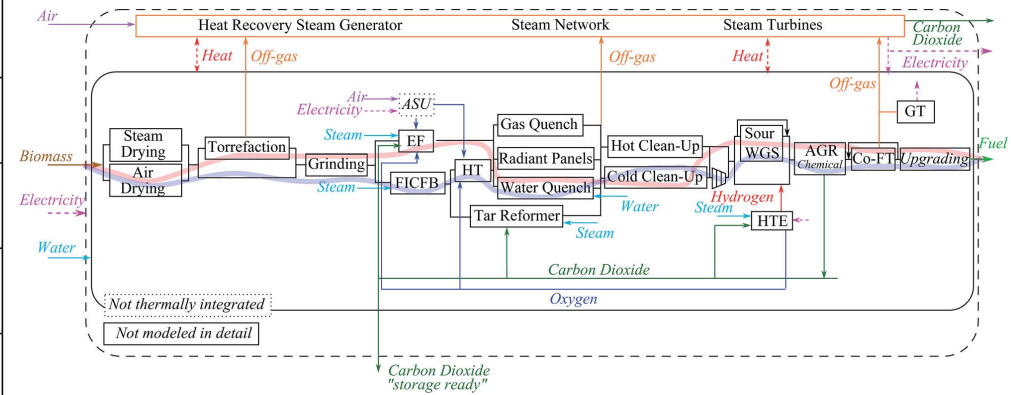
$$\eta_{el} = \frac{\Delta \dot{m} LHV_{FT}}{\Delta \dot{E}} = 0.84$$

Fig. 7 FT fuel production vs. electricity balance (positive if exported, negative if imported) of the optimised solutions presented in Fig. 5.

Liquid fuels



A-T-EF-W-C-WG	+	A-T-EF-G-C-E-CO2	◇
A-T-EF-G-C-WG	×	A-T-EF-G-H-E-CO2	◆
A-T-EF-W-H-WG	*	A-FB-HT-W-C-WG	+
A-EF-G-C-WG	□	A-FB-HT-RP-H-WG	*
S-T-EF-G-C-WG	■	A-T-FB-HT-W-C-WG	□
A-T-EF-W-C-WG-GT	○	S-FB-HT-W-C-WG	■
A-T-EF-G-H-WG-GT	●	A-FB-HT-W-C-WG-GT	○
A-T-EF-W-H-WG-GT	△	A-FB-HT-W-C-E	●
A-T-EF-W-H-WG-GT-FTrec	▲	A-FB-HT-W-C-E-CO2	▽
A-T-EF-G-C-E	▽	A-FB-HT-RP-C-E	△
A-T-EF-W-H-E	▼	A-FB-HT-RP-H-E	▲
A-T-EF-W-C-E	◇	A-FB-R-C	▼
A-T-EF-W-H-E-CO2	◆	A-FB-R-H	◇



Importance of electricity import

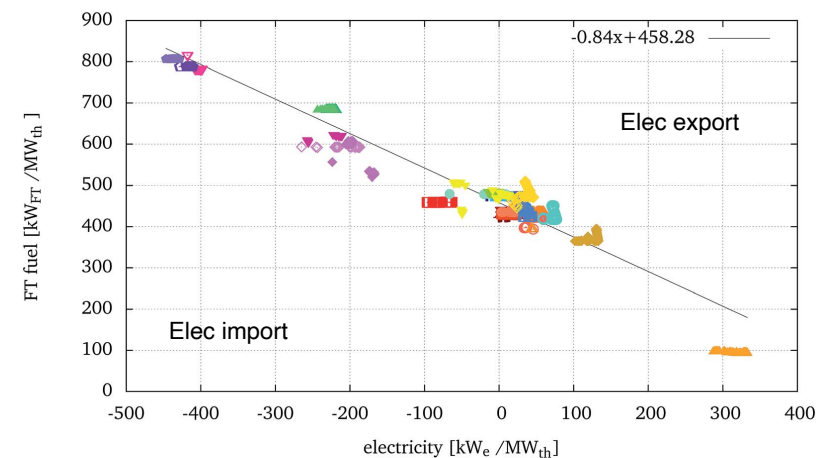
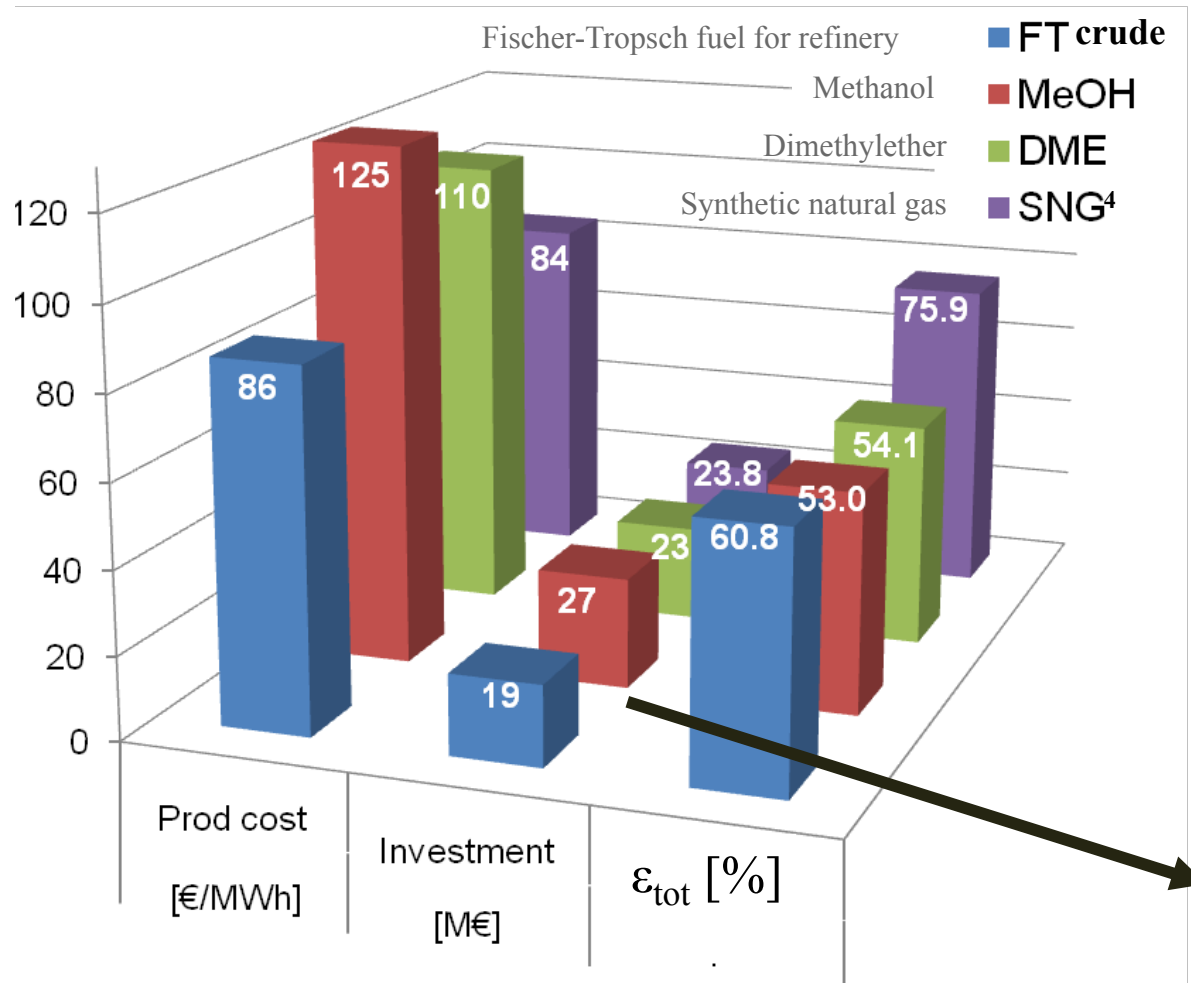


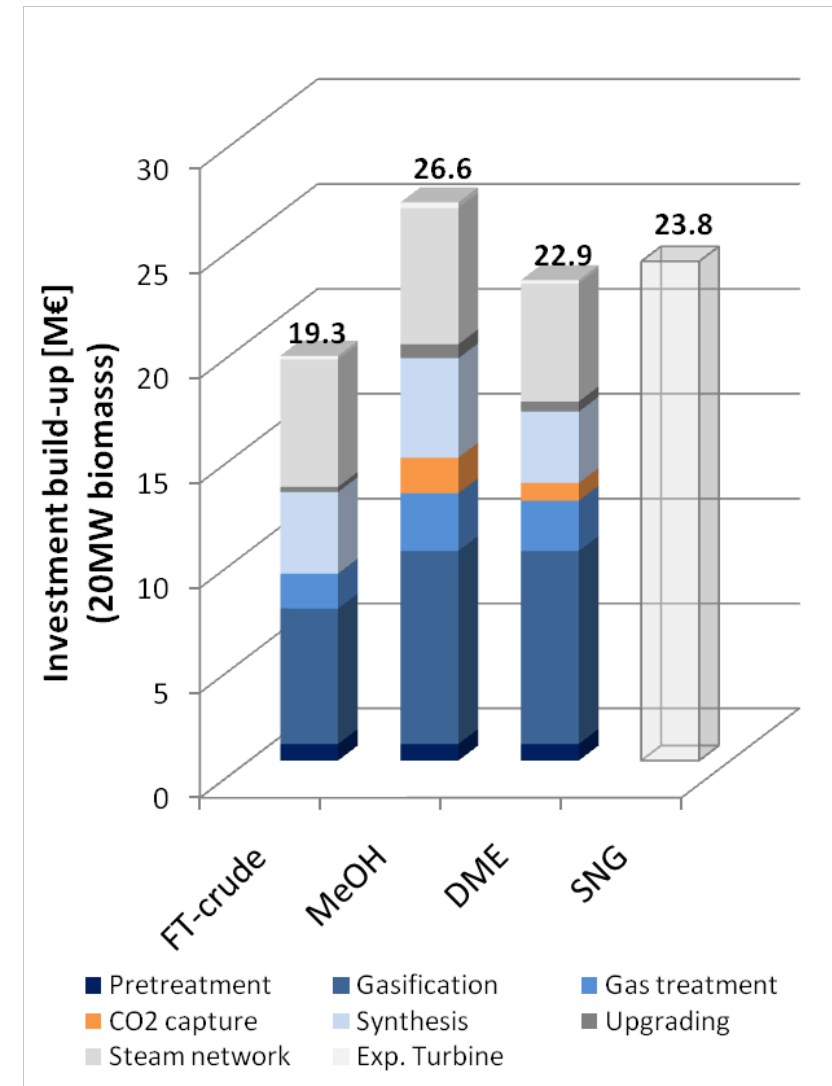
Fig. 7 FT fuel production vs. electricity balance (positive if exported, negative if imported) of the optimised solutions presented in Fig. 5.

Process Performance - Comparison

- ◆ **Base scenario:** indirect fluidized bed gasification, cold gas cleaning

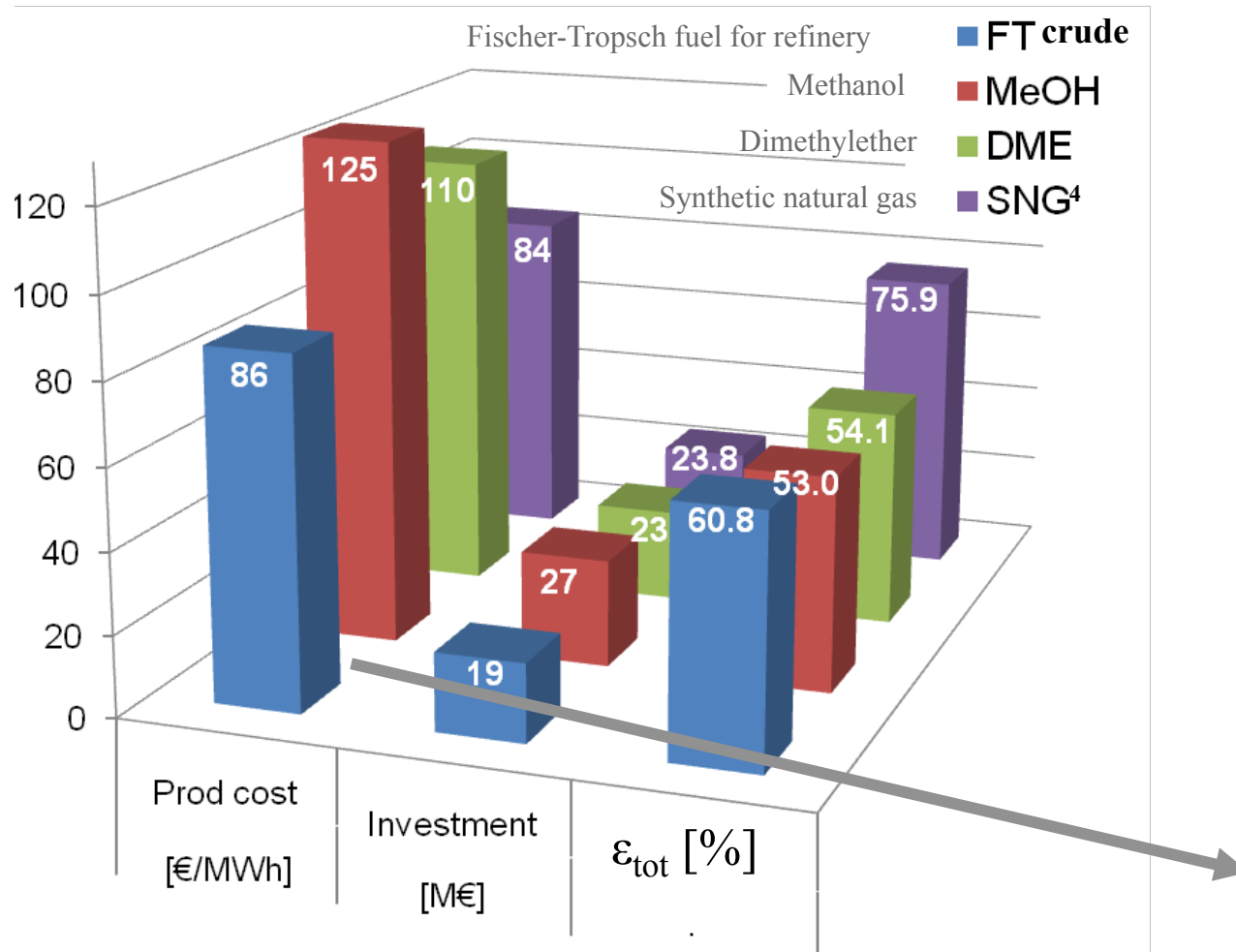


- ➔ **FT process highest performance**
- FT-upgrading not included
 - No CO₂ removal unit required
 - **Power demand variation**

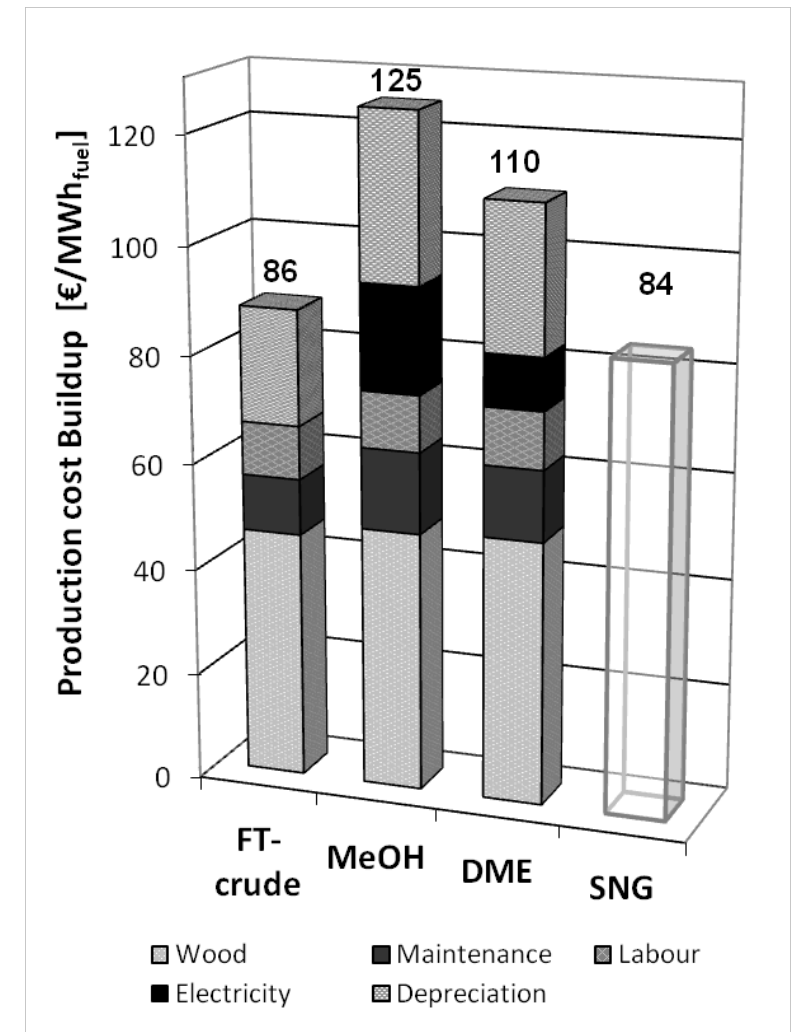


Process Performance - Comparison

- ◆ **Base scenario:** indirect fluidized bed gasification, cold gas cleaning



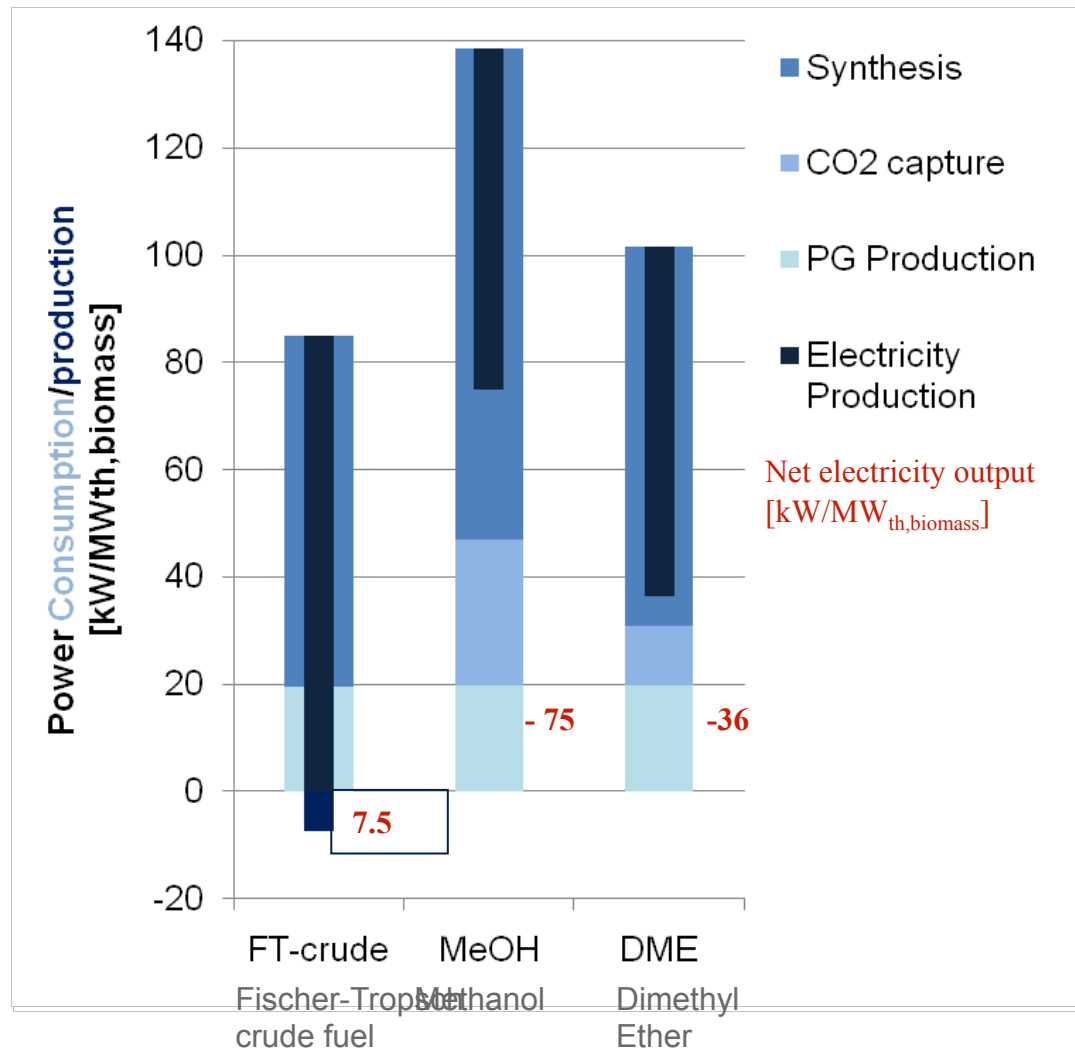
- ➔ **FT process highest performance**
- FT-upgrading not included
 - No CO₂ removal unit required
 - **Power demand variation**



Biomass price: 33 €/MWh^{4,5}
Electricity price: 180 €/MWh^{4,5}

Process Performance - Comparison

◆ Base scenario: Power balance



➔ Power consumption

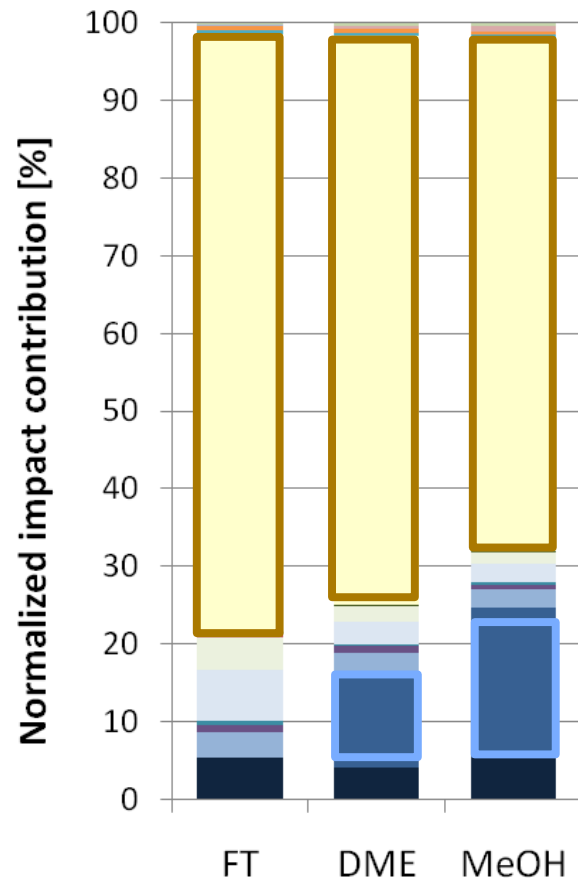
- P_{syn} : FT 25bar, MeOH 85bar, DME 50bar
- CO₂ capture: chemical absorption with MEA

➔ Power production

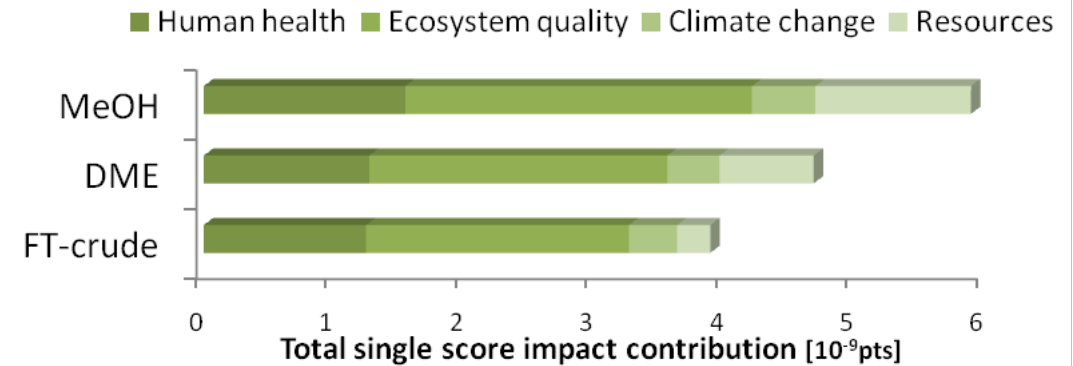
- FT: Electricity output !

Process Performance - Comparison

◆ Competitiveness: Environmental impacts



- Contribution of process equipment
- Transport of wood
- Transport of flows
- charcoal for sorbalit
- Solid waste from gasification
- Zinc catalys
- CO2 from "Oil for starting"
- remaining processes
- Net production or consumption of electricity
- Empty lorries
- olivine for CFB gasification
- oil for saring gasification
- Rape methyl ester for scrubbing
- Gypsum from gas cleaning
- Monoethanolamine for CO2 removal



➔ Major differences

- **Electricity consumption**
(Swiss mix for medium voltage electricity production at grid)

➔ Largest impact

- Gas cleaning:
Rape methyl ester (RME) from rape cultivated with pesticides !

➔ Process improvements: Alternative gas cleaning technologies

- Liquid fuel => energy density up to 40 MJ/kg/32 MJ/l
- Biomass 2 Liquid => 50- 60%
 - including co-production of electricity
- Liquid fuels
 - *** FT fuels => integration to refining
 - ** Methanol => fuel or product
 - * DME => green substitute fuel/additive
- Stoichiometry => production of H₂ by electrolysis
 - marginal efficiency is 84% Electricity to LHV