IEA Bioenergy
Technology Collaboration Programme

Case studies

on green hydrogen in bio-based processes

Nicolaus Dahmen

Berlin, IEA Expert workshop, March 29, 2023

Expectations at the example of biomass gasification based fuels

Lignocellulose gasification	$C_6H_8O_4 + 2\ O_2 \rightarrow 5.2\ CO + 2.8\ H_2 + 0.8\ CO_2 + 1.2\ H_2O$
Water-gas-shift	$2.5\ CO + 2.5\ H_2O \leftrightarrows 2.5\ CO_2 + 2.5\ H_2$
Sum after shift	$C_6H_2O_4 + 2\ O_2 \rightarrow 2.7\ CO + 5.3\ H_2 + 3.3\ CO_2$
BtL synthesis	$2.7\ CO + 5.3\ H_2 \rightarrow 2.7\ \text{“}CH_2\text{“} + 2.7\ H_2O$
RWGS	$3.3\ CO_2 + 3.3\ H_{2,ext} \leftrightarrows 3.3\ CO + 3.3\ H_2O$
PtL synthesis	$3.3\ CO + 6.6\ H_{2,ext} \rightarrow 3.3\ \text{“}CH_2\text{“} + 3.3\ H_2O$
PBtL	$C_6H_8O_4 + 2\ O_2 + 10\ H_{2,ext} \rightarrow 6\ \text{“}CH_2\text{“} + 8\ H_2O$
Water electrolysis	$10\ H_2O \leftrightarrows 10\ H_2 + 5.5\ O_2$

- Hydrocarbon yield may be doubled!
- Oxygen by-produced sufficient for autothermal gasification
- Other examples available e.g. from biotech conversions

First estimates on H_2 boosted bioliq process with FT synthesis

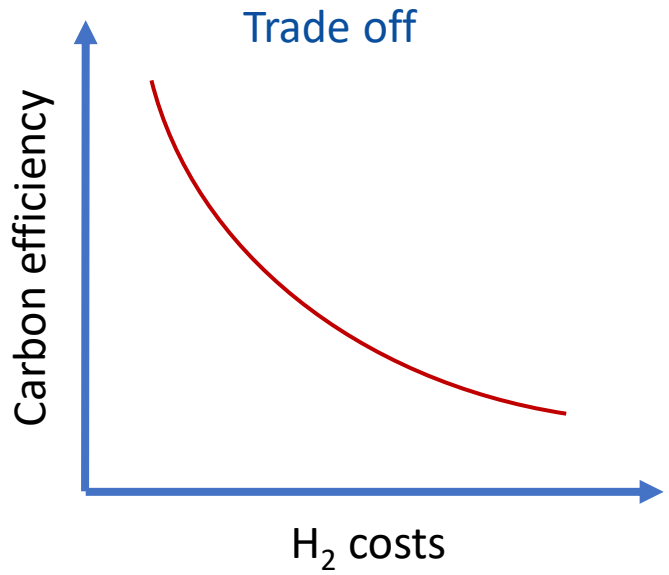
- Thermal fuel capacity: 110 MW_{th}
- Share of electricity costs: 50.7 %
- Full heat integration and export

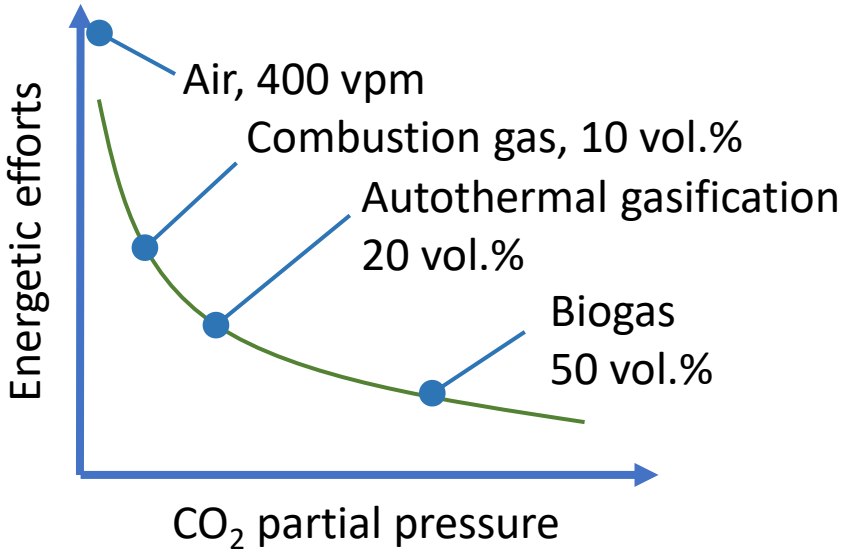
	BtL	PBtL	PtL, max	PBtL, min
Product capacity / MW	32.6	123.3	123.5	32.7
Fuel efficiency	29.8 %	45 %	46.2 %	
Overall efficiency	63.0 %	56.6 %	62.4 %	
Carbon conversion	24.9 %	97.7 %	99 %	
Net production cost / EUR/L_{ge}	2.05	2.15	2.75	2.64

F. Albrecht et al.,
Fuel 194 (2017)

Statements for discussion

- Different process pathways and even process variants can benefit to variable extent from hydrogen supply
- Economics may be determined by the carbon conversion vs. costs trade-off and/or other optimization criteria
- Carbon dioxide available in different partial pressure and purity





Options for hydrogen integration

Gasification based processes

- Carbon dioxide capture and reverse-water-gas-shift reaction
- Addition of hydrogen to gasification of biomass
- Addition of hydrogen to fuel synthesis

Pyrolysis/HTL based processes

- Addition of hydrogen in-situ during (catalytic) hydro-pyrolysis/solvolysis
- Hydro-treatment of pyrolysis vapors
- Hydro-treatment of bio-oils/-crude
- Carbon dioxide capture and reverse-water-gas-shift reaction

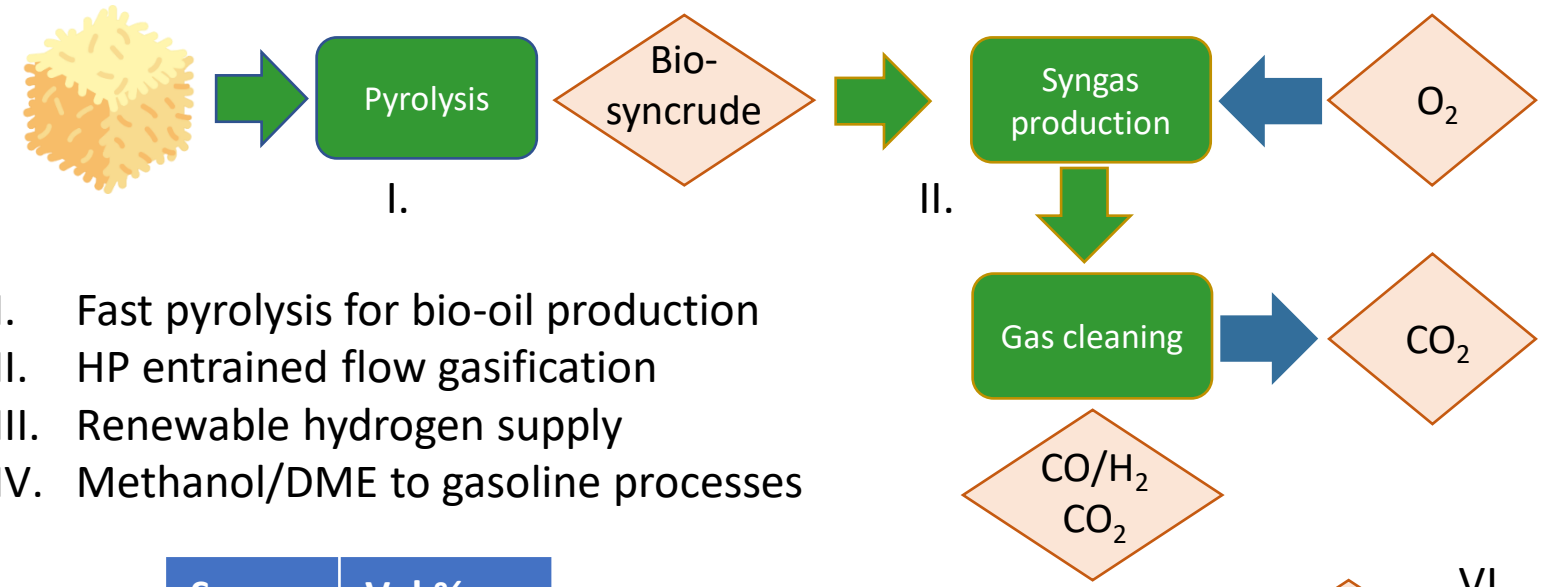
Microbial processes

- Carbon dioxide capture and reverse-water-gas-shift reaction

H_2 boosted bioliq process with MtG

Addition of H_2 to synthesis

reFuels



I. Fast pyrolysis for bio-oil production
II. HP entrained flow gasification
III. Renewable hydrogen supply
IV. Methanol/DME to gasoline processes

Syngas	Vol.%
CO	36.0
H_2	35.0
CO_2	18.0
CH_4	2.0
H_2O	6.0

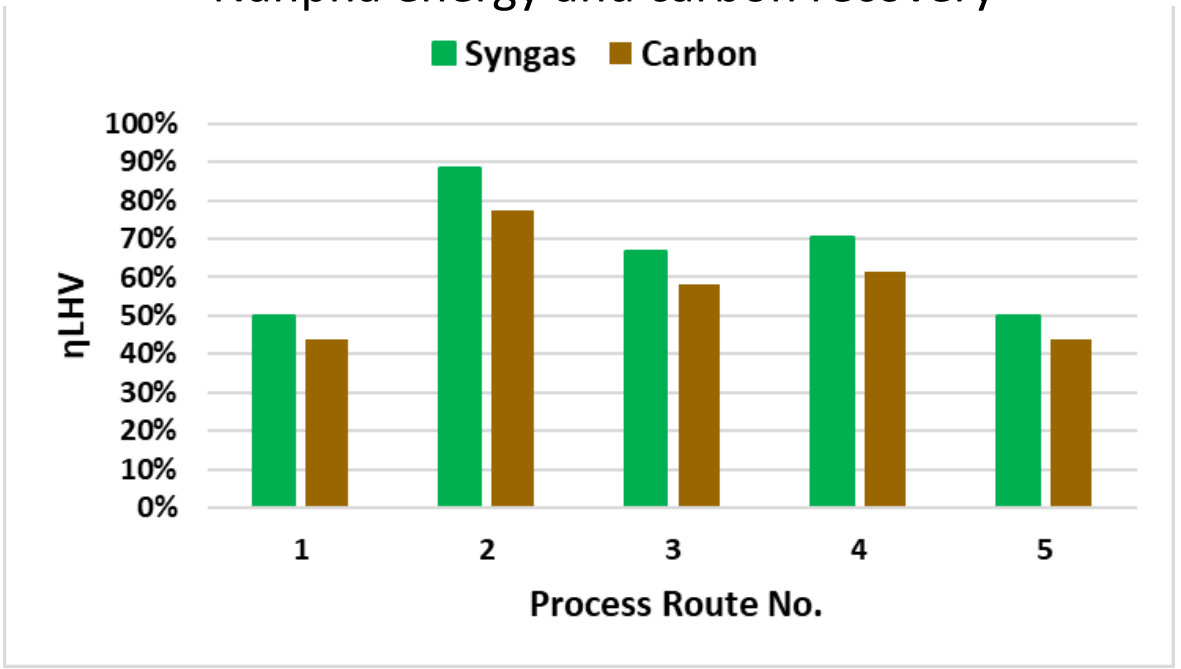
H_2 boosted bioliq process with MtG

Addition of H_2 to synthesis

ReFuels

- Gasoline production from biomass based syngas ($CO/H_2 \cong 1$) via different pathways via Methanol and/or DME, with/without external H_2
- Simulations with kinetic models validated by data from industrial plants
- In total, synthesis via MeOH can most benefit from H_2 addition, while MtG via DME performs better without H_2 supply.

Nahpha energy and carbon recovery



1: via one step MeOH synthesis
2: via one step MeOH + external H_2
3: via one step DME synthesis
4: via one step DME + external H_2
5: two step MeOH/DME synthesis

M. Ebrahimi, KIT-IKFT

H_2 boosted bioliq process with MtG

Addition of H_2 to synthesis

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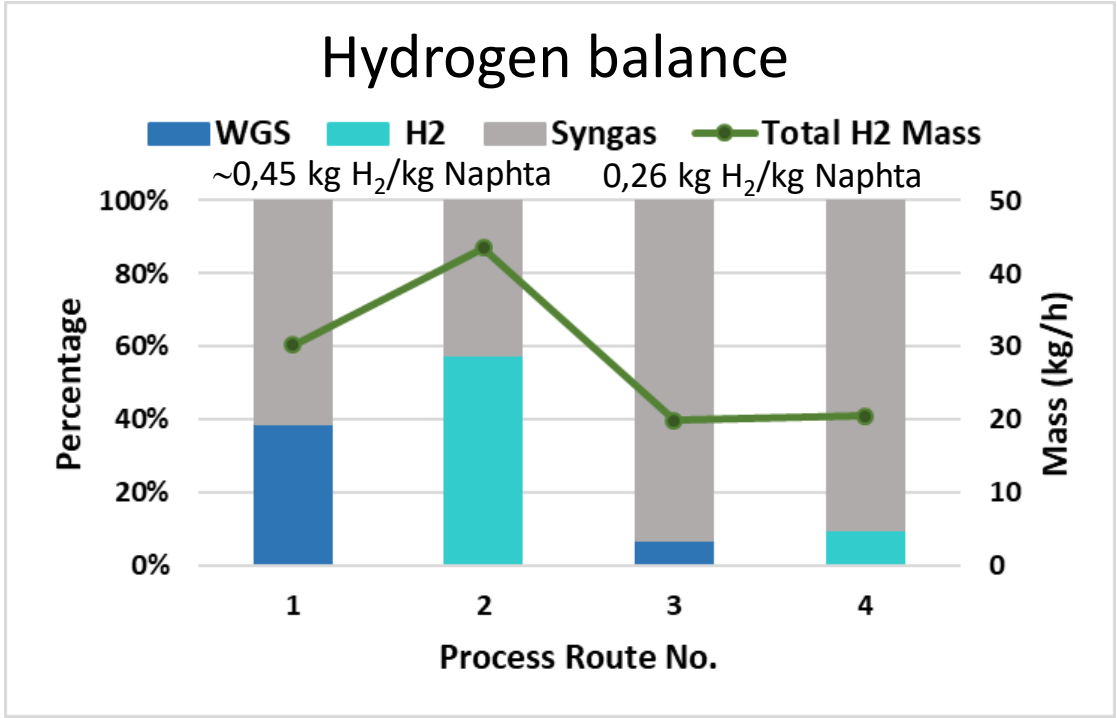

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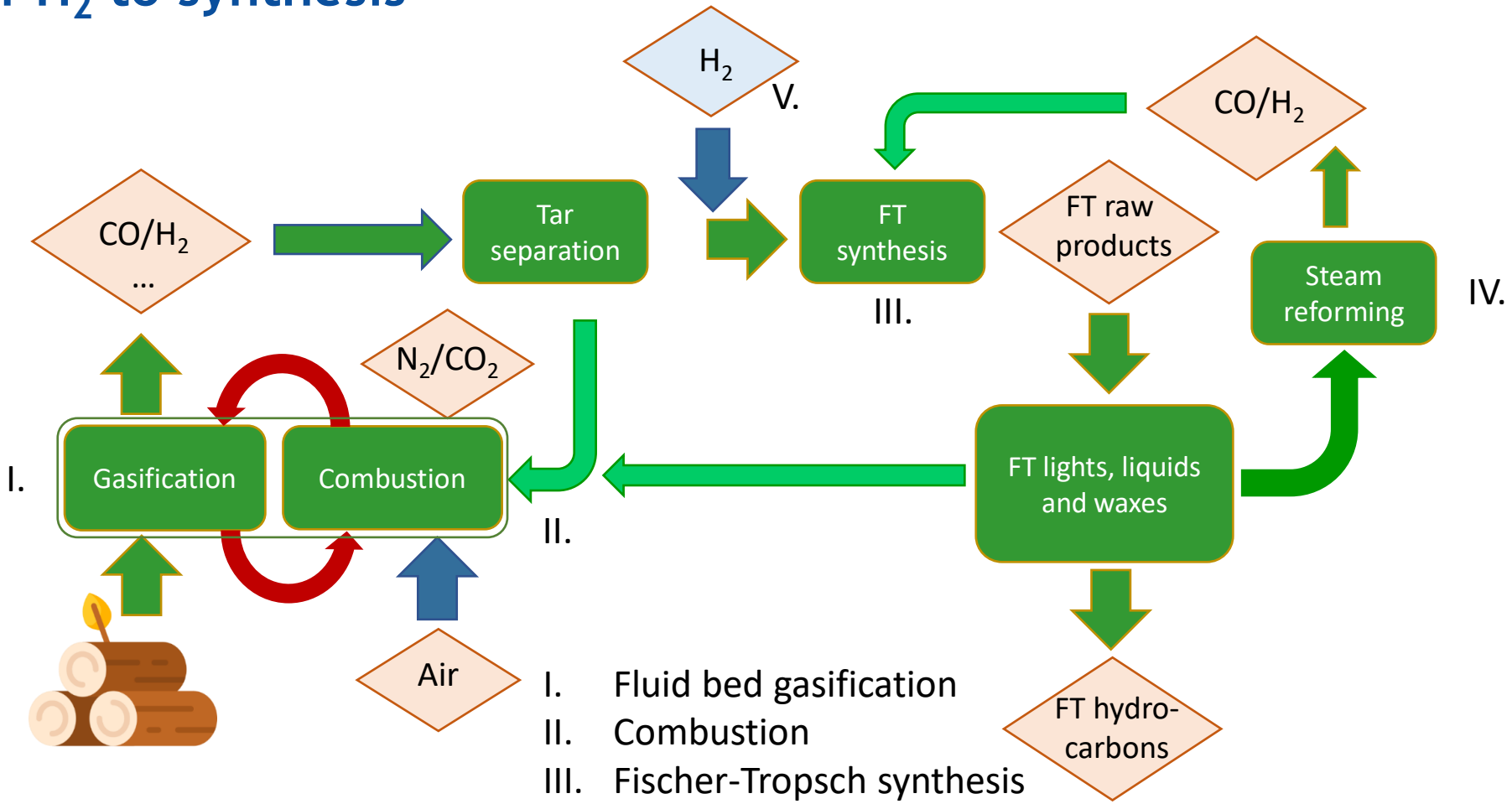
M. Ebrahimi, KIT-IKFT

Direct biomass gasification for FT-products

Addition of H_2 to synthesis

HELMHOLTZ CLIMATE INITIATIVE

Syngas	Vol.%
CO	24.3
H_2	50.9
CO_2	16.5
CH_4	6.5
H_2O	< 1



I. Fluid bed gasification
II. Combustion
III. Fischer-Tropsch synthesis
IV. Steam reforming
V. External hydrogen supply

Hi-CAM final report

D. Wiegand, R. Rauch, KIT-EBI

Direct biomass gasification for FT-synthesis

Addition of H_2 to synthesis

HELMHOLTZ CLIMATE INITIATIVE

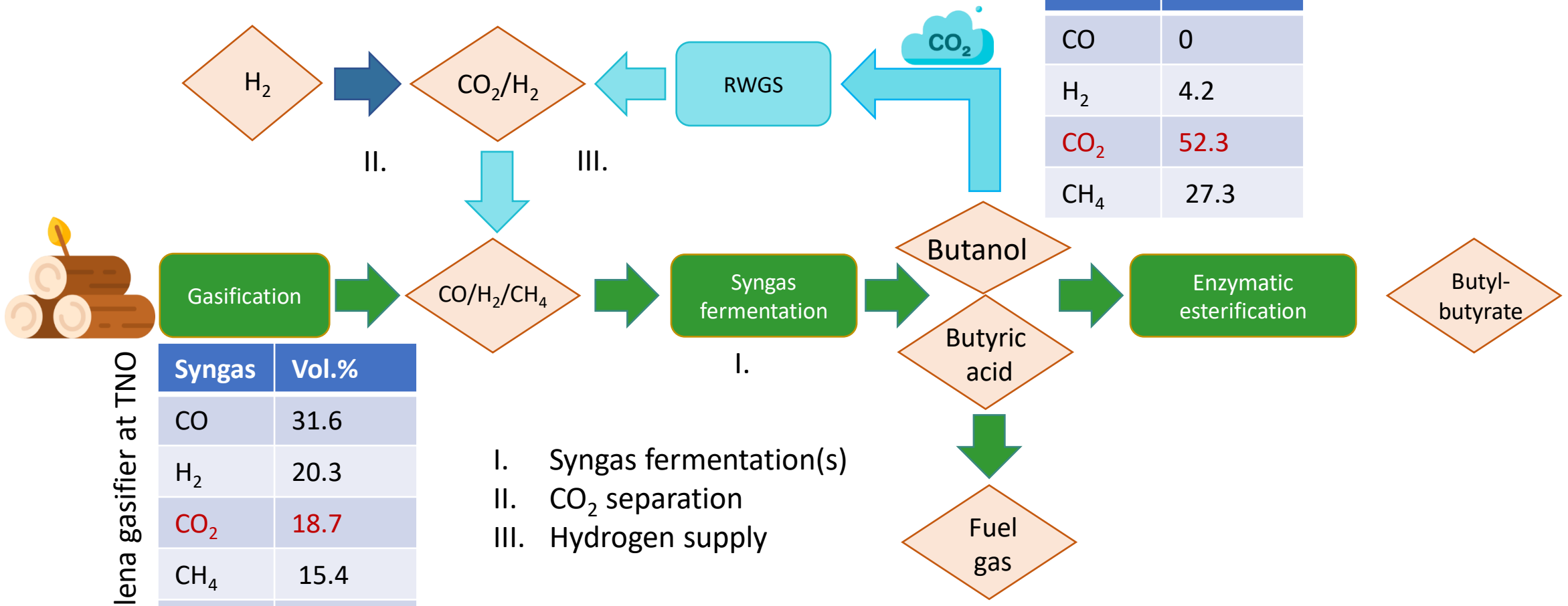
- Direct gasification of biomass dual fluid bed concept
- Cold gas efficiency ca. 82 %, scaled to 100 MW_{th} (38.7 t/h)
- 1/3 CO_2 in syngas, 2/3 in combustion flue gases
- Hydrogen addition to FT-synthesis via kinetic model

	BtL	H_2 supply
Gasification capacity / MW	100	100
Fuel efficiency*	51 %	53.5 %
Overall efficiency with heat use	63 %	62 %
Carbon conversion	31.2 %	38.3 %
Hydrocarbon production capacity	500 kg/h	814 kg/h

*related to biomass+H_2 input

D. Wiegand, R. Rauch, KIT-EBI
Hi-CAM final report

Syngas fermentation to C_4- and C_8-hydrocarbons
Addition of H_2 to fermentation gas



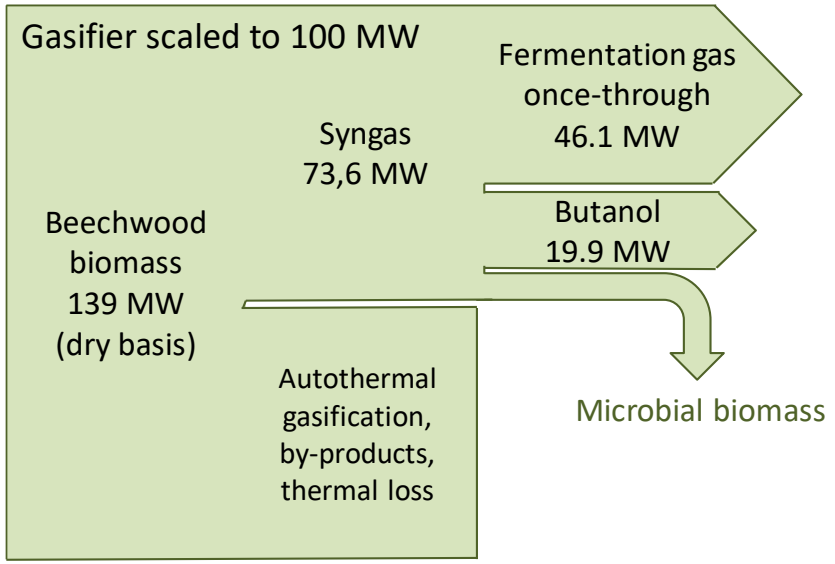
Gas	Vol.%
CO	0
H_2	4.2
CO_2	52.3
CH_4	27.3

Syngas	Vol.%
CO	31.6
H_2	20.3
CO_2	18.7
CH_4	15.4
H_2O	4.8

I. Syngas fermentation(s)
II. CO_2 separation
III. Hydrogen supply

Energy balance from syngas fermentation
Addition of H_2 to fermentation gas

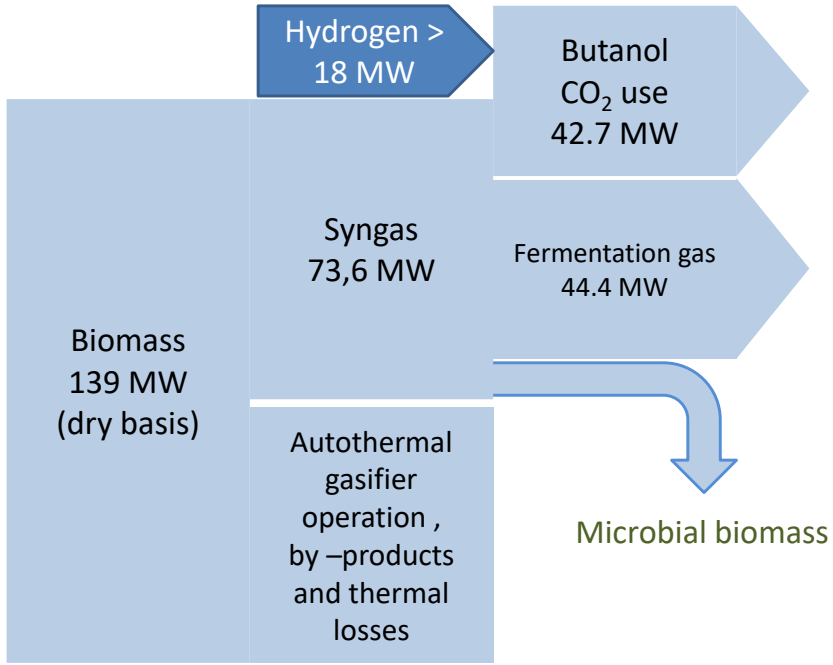
Case 1: Once through



C-recovery:
21.2 % beechwood
17.0 % lignin

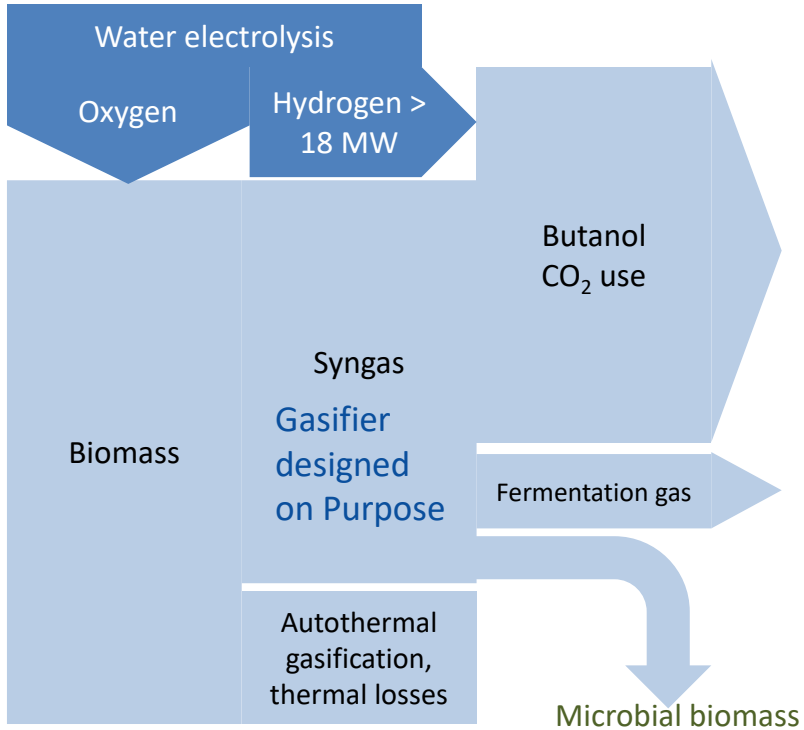
Case 2: CCU

Specific production cost reduce by 50% when increasing the yields by a factor of 4!



74.1 % beechwood
79.3 % lignin

Further improvment?!



AMBITION final report; ambition-research.eu

Options for CO_2 activation

reFuels

H_2 and CO_2 integration via

- Reverse-water-gas-shift reaction (TRL 6)
- Electrochemical reduction to syngas or olefins (TRL <6)
- CO_2-methanation and dry-gas reforming (TRL >6, licensible)

	Methanation and DGR	RWGS	Co-SOEC
C utilization	61 %	85 %	100 %
CO_2 reduction	7,3 t/h	12,5 t/h	14,2 t/h
Product capacity	20.400 t/a	27750 t/a	38500 t/a
Energy recovery	42 %	50 %	52 -55 %

Case study: Refinery integrated FT demo plant with 100 MW electrolysis for diesel and jet fuel production

Concluding statements

- Power enhanced BtL processes are promising: They combine “energetic” bio-carbon with “zero-energy” CO_2 utilization allowing to maximise C-conversion
- In optimum cases increased effort including H_2 supply is compensated by increase in yield
- Hydrogen supplied directly to gasification or synthesis cannot utilize all CO_2 formed during the process
- CO_2 capture is, but RWGS is not state-of-the-art today


Bioliq and Energy Lab, KIT
Thank you!

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