



Process Modelling of Biofuel Production from Contaminated Biomass Through Entrained Flow Gasification and Syngas Fermentation



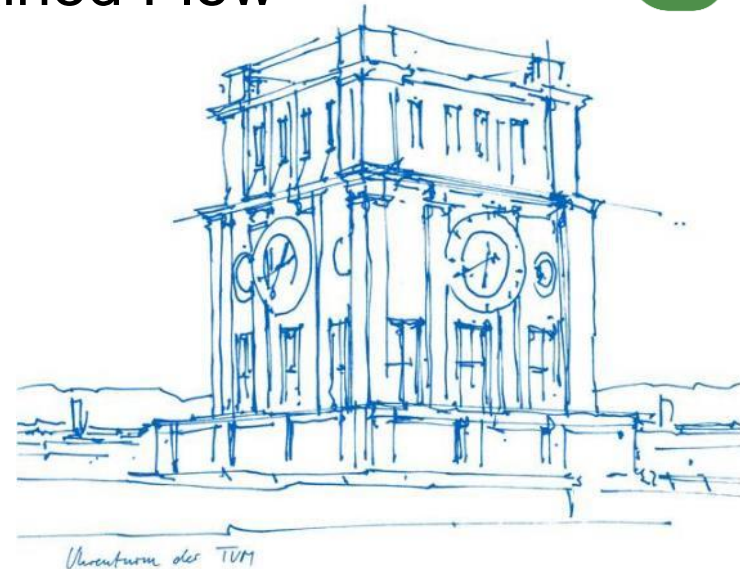
Marcel Dossow

Technical University of Munich

Department of Mechanical Engineering

Chair of Energy Systems

Bologna, 5th June 2023



Agenda

Project GOLD

Process modelling in Aspen Plus

Syngas Fermentation Modelling in Aspen Plus

Process Model Development in Aspen Plus

Results & Discussion

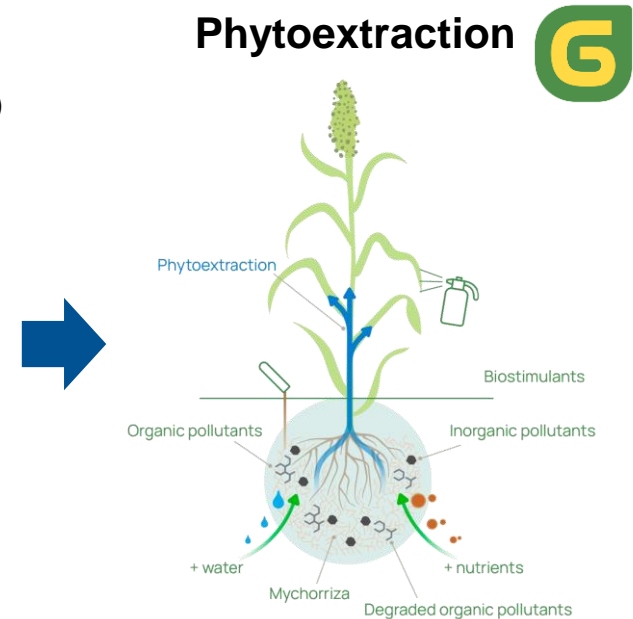
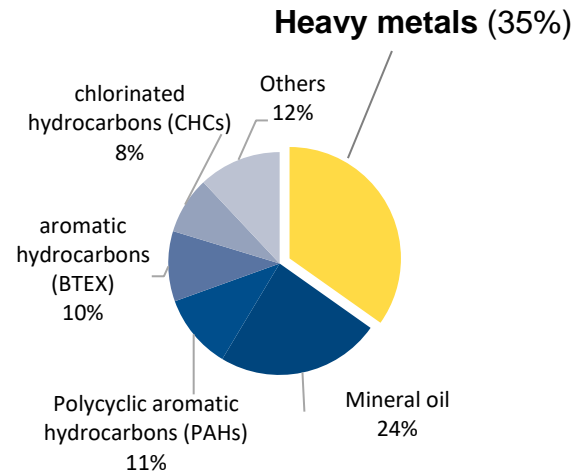
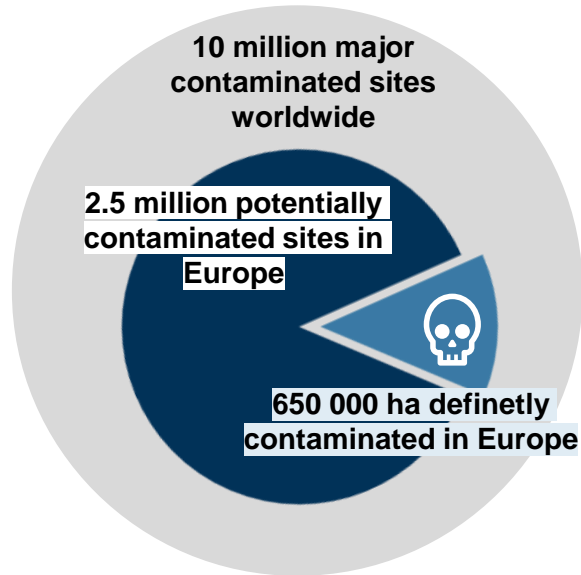
Conclusion & Outlook

GOLD



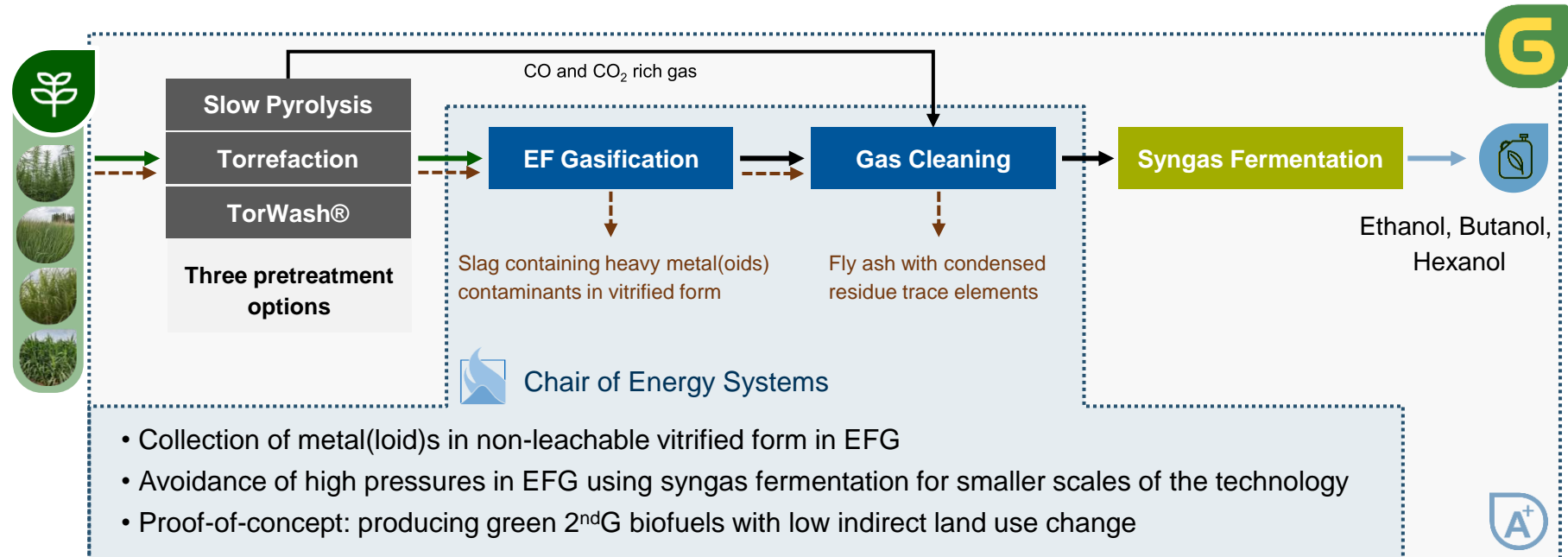
Contaminated soils and phytoremediation

Motivation and GOLD project Idea

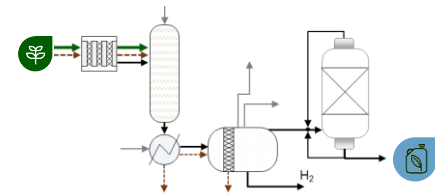


Conversion processes for clean liquid biofuel production

High temperature gasification with syngas fermentation



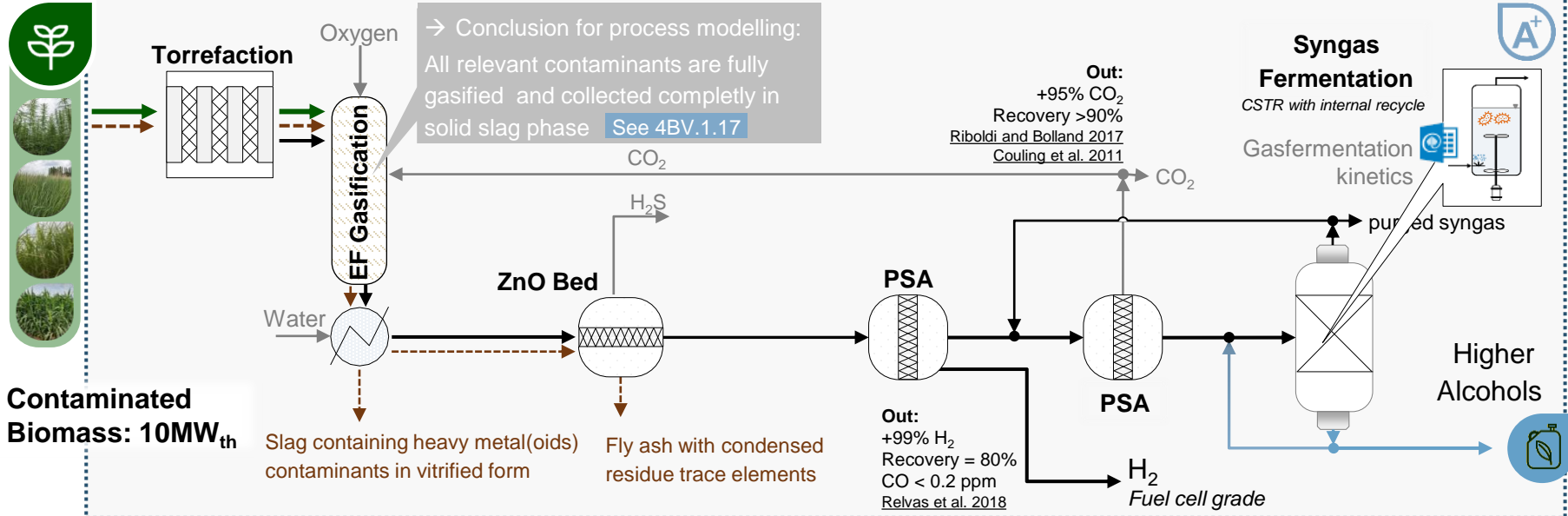
- Collection of metal(loid)s in non-leachable vitrified form in EFG
- Avoidance of high pressures in EFG using syngas fermentation for smaller scales of the technology
- Proof-of-concept: producing green 2ndG biofuels with low indirect land use change

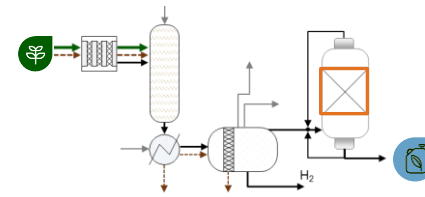


Conversion processes for clean liquid biofuel production

Process and gas phase modelling

→ Comparison of process options

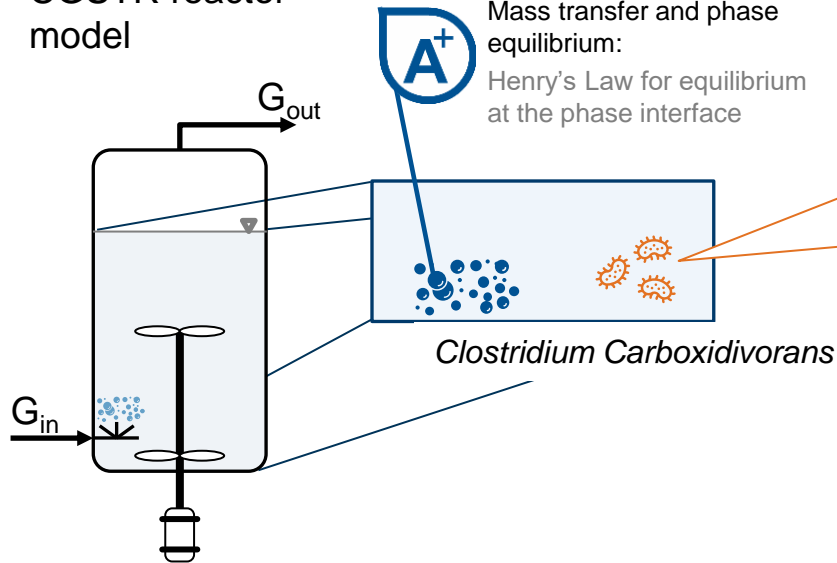




Syngas fermentation model

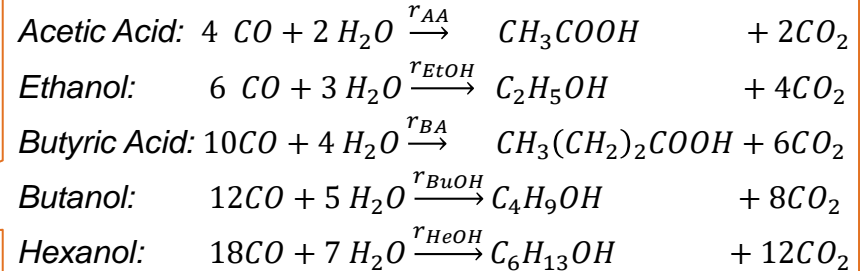
Reaction kinetics inside C(G)STR

CGSTR reactor model

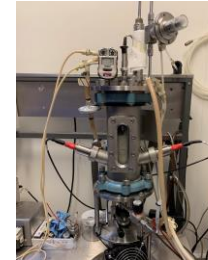


Reactions implemented in (G)CSTR

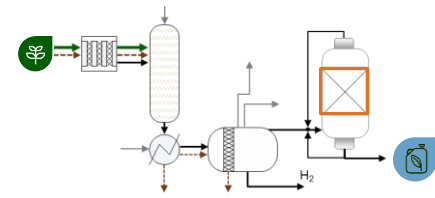
MO first consumes CO before $CO_2 + H_2O$



Model fit to data from Doll 2018
 Data set limited to continuously gassed stirred tank reactor with different CO input partial pressures



Syngas fermentation lab @TUM-CBE



Syngas fermentation model

Reaction kinetics inside C(G)STR

Gasfermentation kinetics for *C. carboxidivorans*

Reaction rate law derived for each reaction:

$$r_i = \nu_i \cdot r = -\frac{d\dot{n}_i}{dt}$$

$$r_i = k_i \cdot \frac{c_{CO}}{c_{CO} + \sum (K_{i,j} \cdot c_{P,j}^{w_j})}$$

Labels for the equation above:
 - Kinetic factor: k_i
 - Variable CO concentration: c_{CO}
 - Substrate inhibition term: c_{CO}
 - Product inhibition term: $\sum (K_{i,j} \cdot c_{P,j}^{w_j})$



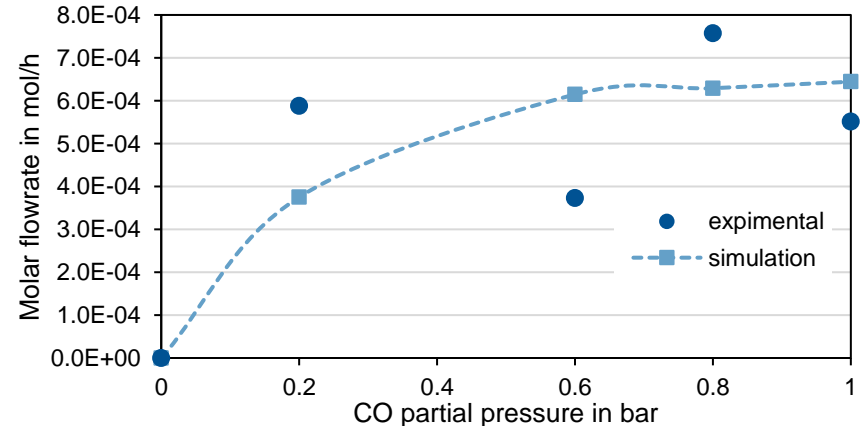
Aspen Plus LHHW expression:

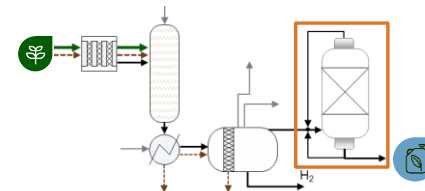
$$r = \frac{(\text{kinetic factor})(\text{driving force expression})}{(\text{adsorption term})} = (kT^n e^{-\frac{E}{RT}}) \frac{k_1 \prod c_i^{\alpha_i} - k_2 \prod c_j^{\beta_j}}{[\sum_{i=1}^M K_i (\prod c_j^{\nu_j})]^m}$$

Example: acetic acid: $4 CO + 2 H_2O \rightarrow CH_3COOH + 2CO_2$

$$r_{AA} = 1.70 \cdot 10^{-7} \frac{\text{kmol}}{\text{s} \cdot \text{m}^3} \cdot \frac{c_{CO}}{c_{CO} + c_{P,AA}^3 + \sum (0.1 \cdot c_{P,j}^4)}$$

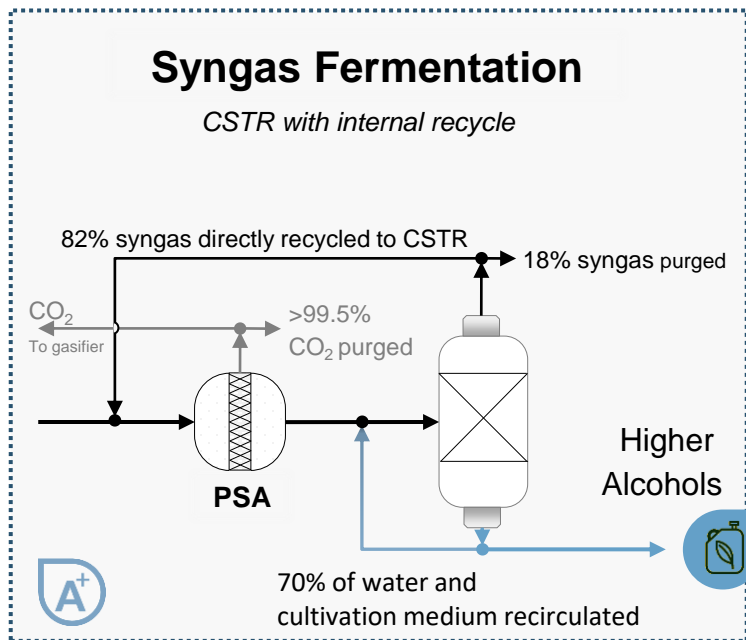
Data fit: acetic acid





Syngas fermentation model

Process modelling



Reactor conditions

$p = \text{const} = 1 \text{ bar}$

$T = \text{const} = 37 \text{ }^\circ\text{C}$

$\text{pH} = \text{const} = 6$

$\tau_l = 8h, \tau_g = 1h$

For 95% CO conversion: $V_R = 4800 \text{ m}^3$



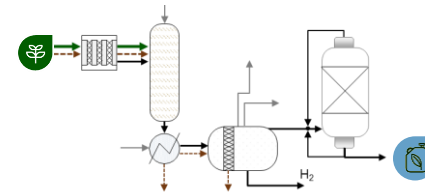
Large-scale fermentation:

CSTRs in industry: up to 300 m^3

Spec. power input $2 \text{ kW}_{el}/\text{m}^3$

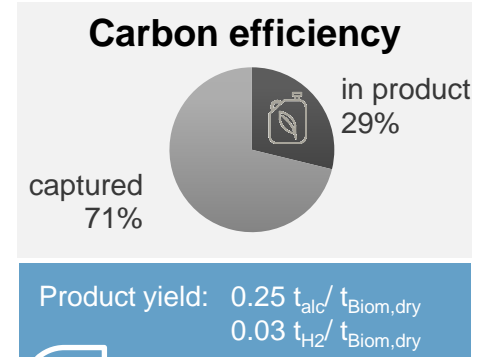
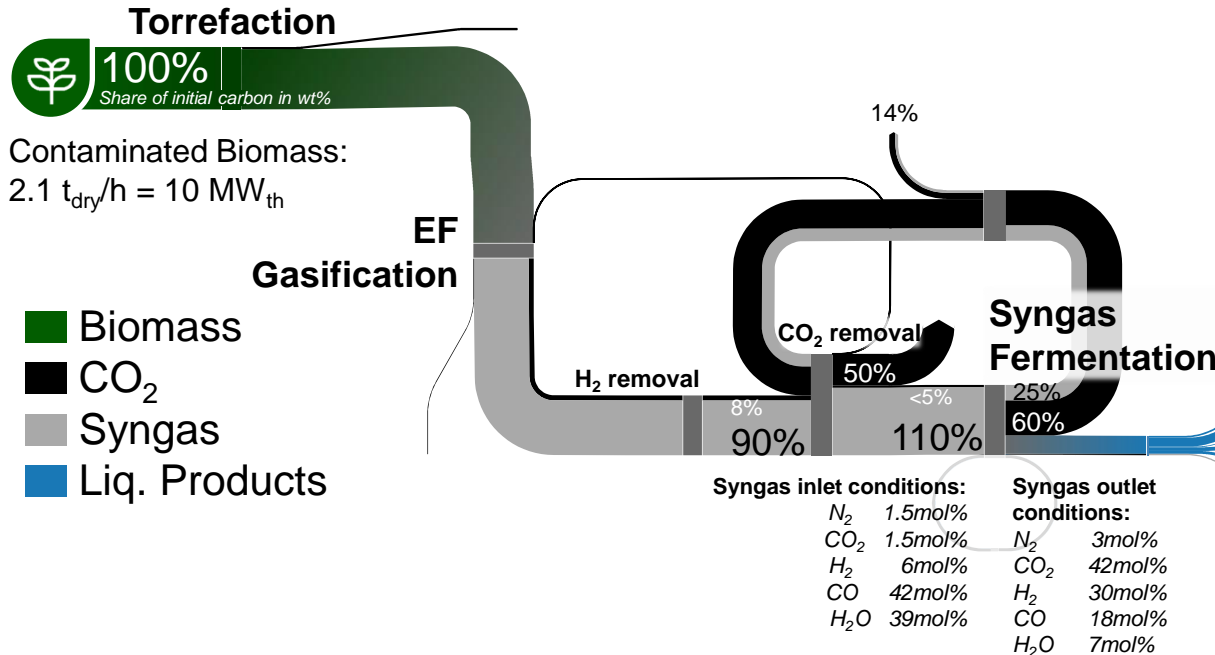
→ Installed stirrer power: $\sim 10 \text{ MW}_{el}$

Meyer et al. 2016: Industrial-Scale Fermentation

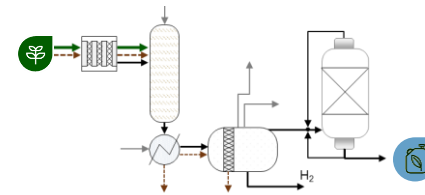


Process and gas phase modelling

Carbon flow diagram and carbon efficiency

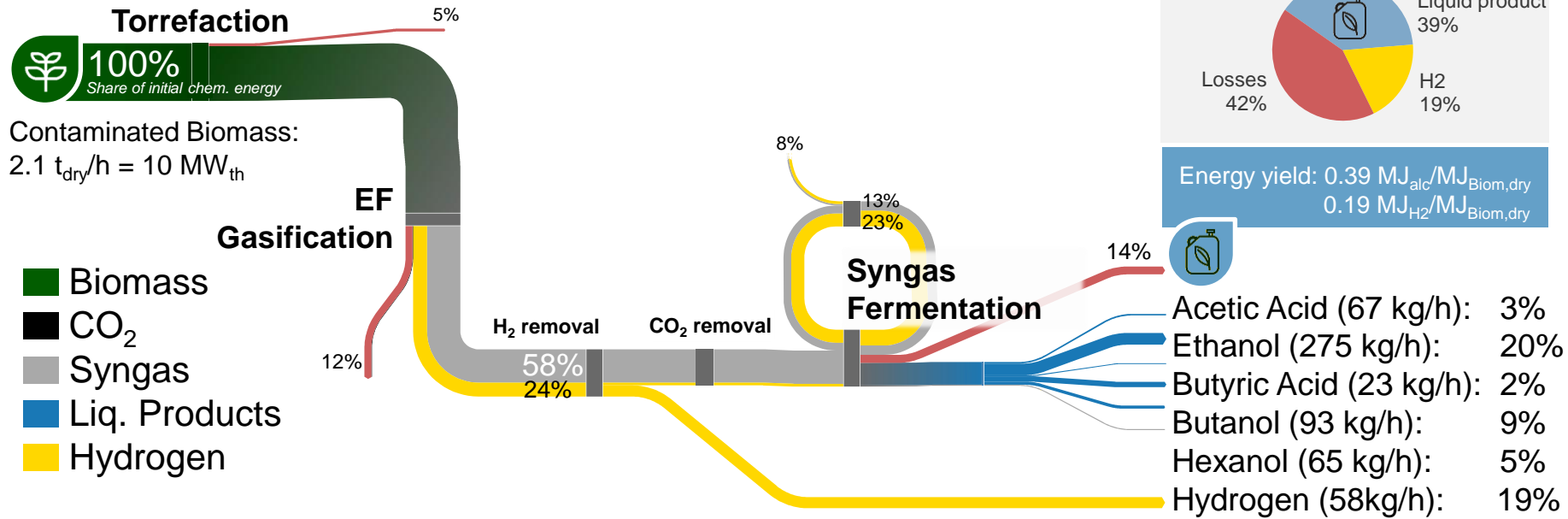


- Acetic Acid (67 kg/h): 3%
- Ethanol (275 kg/h): 14%
- Butyric Acid (23 kg/h): 1%
- Butanol (93 kg/h): 6%
- Hexanol (65 kg/h): 5%



Process and gas phase modelling

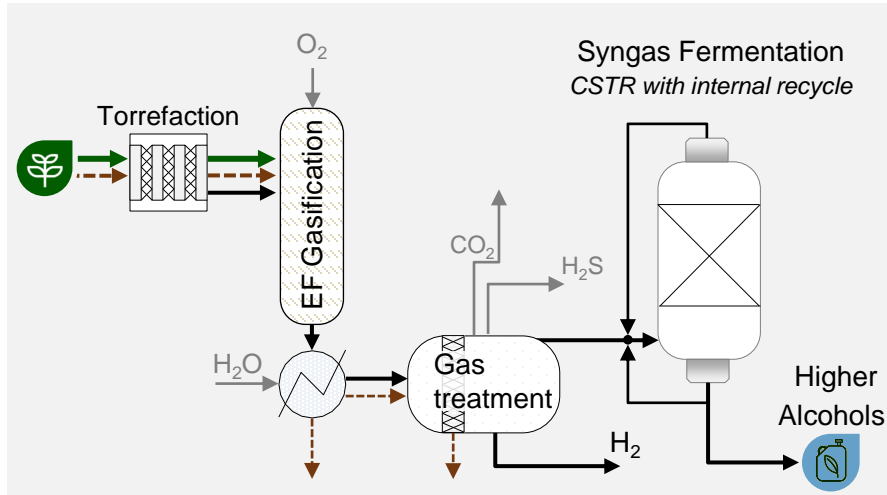
Energy flow diagram and energy efficiency



Conversion processes for clean liquid biofuel production

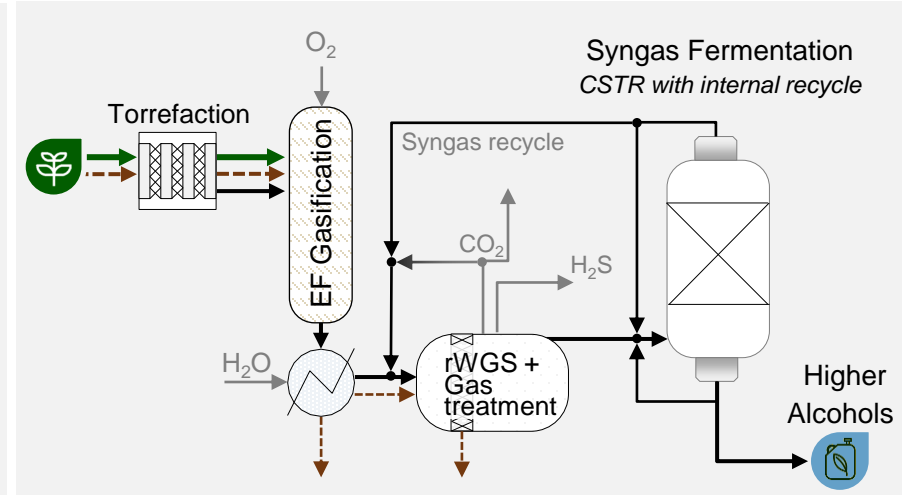
Process comparison

“Once-through” process



→ Green Hydrogen as by-product

Integrated process

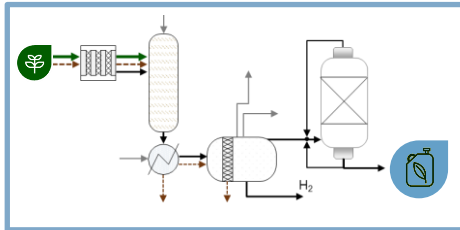


→ Integrating process steps to increase liquid yield

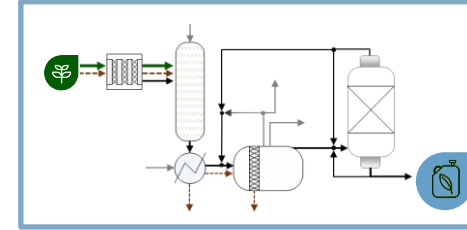
Conversion processes for clean liquid biofuel production

Summary

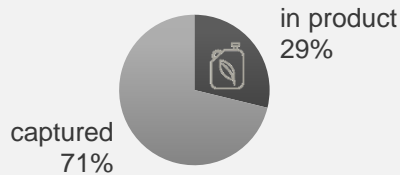
“Once-through” process



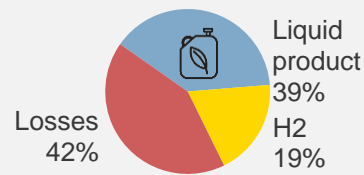
Integrated process



Carbon efficiency



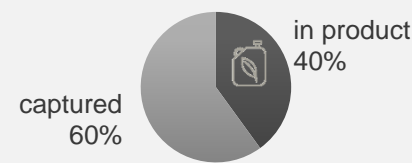
Energy yield



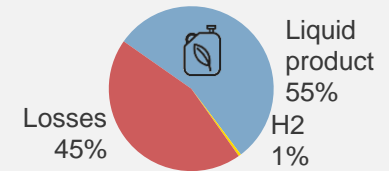
Product yield: $0.25 \text{ t}_{\text{alc}} / \text{t}_{\text{Biom,dry}}$
 $0.03 \text{ t}_{\text{H}_2} / \text{t}_{\text{Biom,dry}}$

Energy yield: $0.39 \text{ MJ}_{\text{alc}} / \text{MJ}_{\text{Biom,dry}}$
 $0.19 \text{ MJ}_{\text{H}_2} / \text{MJ}_{\text{Biom,dry}}$

Carbon efficiency



Energy yield



Product yield: $0.35 \text{ t}_{\text{alc}} / \text{t}_{\text{Biom,dry}}$
 almost no H_2

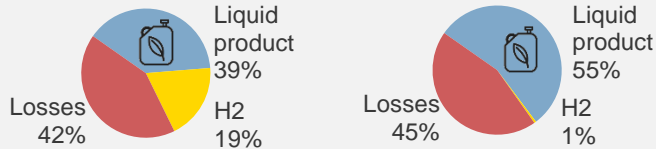
Energy yield: $0.55 \text{ MJ}_{\text{alc}} / \text{MJ}_{\text{Biom,dry}}$
 $0.01 \text{ MJ}_{\text{H}_2} / \text{MJ}_{\text{Biom,dry}}$

Conversion processes for clean liquid biofuel production

Conclusion

Process modeling shows huge potential of novel gasification + syngas fermentation process

Green Hydrogen as by-product, or integrated process with increased liquid yield



- Choice of process option according to boundary conditions
- High power requirement for CSTR
- High selectivity towards ethanol

Outlook

GOLD

- Real biomass fuel analysis data
- Pretreatment data from partners
- Gasification data from own experiments
- Effect of e.g. NH_3 concentrations or contaminants in syngas fermentation

↓ TEA

- Bubble column reactor + cascade reactor network and integration to further increase efficiency
- Pressurized operation? rWGS + CO_2 separation?
- Combination with other syntheses

➔ **Maximizing feasibility**

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Marcel Dossow
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Thank you for your attention

Any questions?

Coordinated by:



www.gold-h2020.eu



Horizon 2020
European Union funding
for Research & Innovation

Partners:



Imperial College
London



INRAE



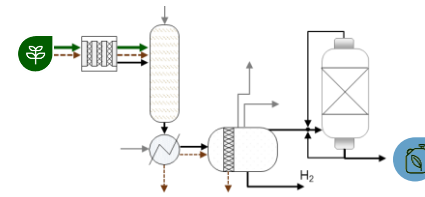
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TNO innovation
for life

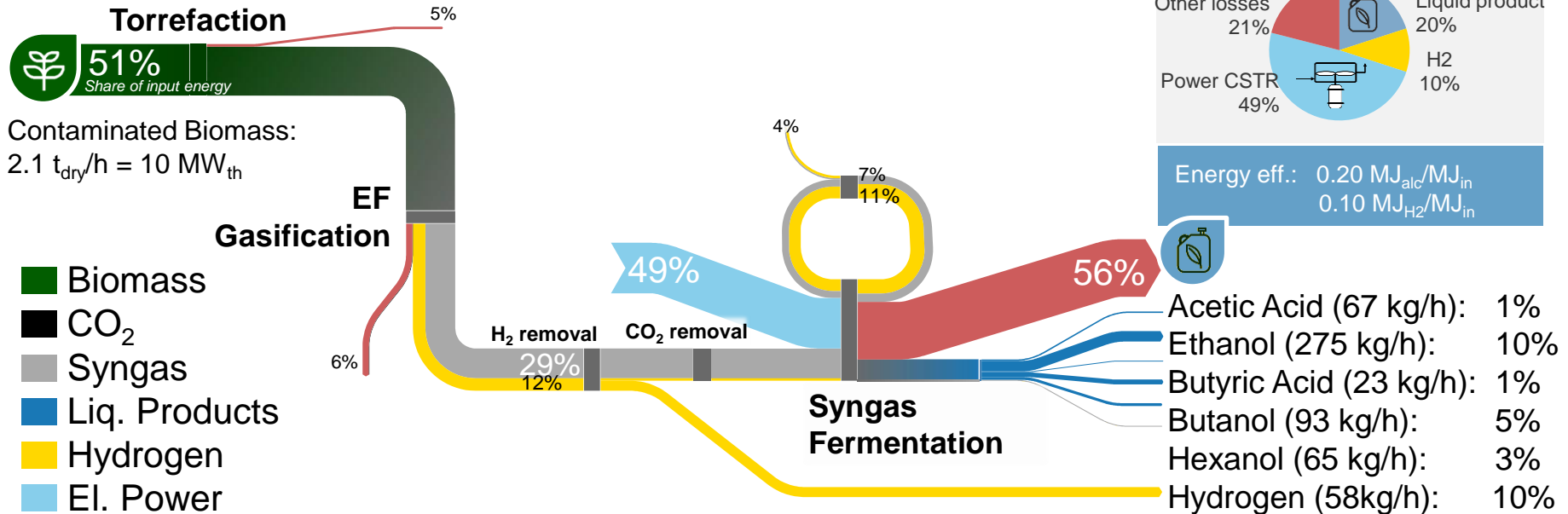
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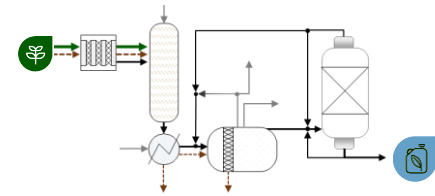




Process and gas phase modelling

Energy flow diagram and energy efficiency

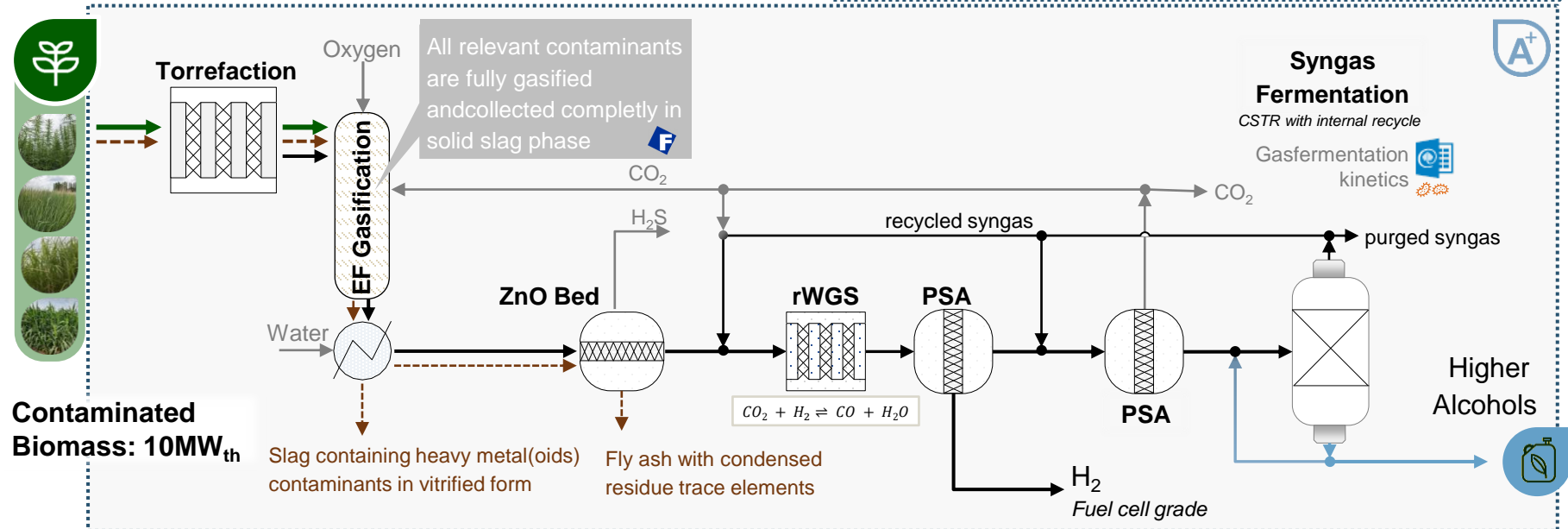


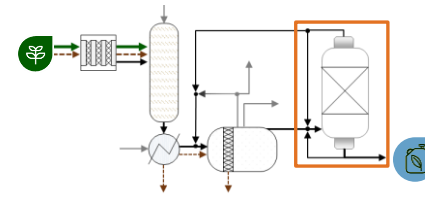


Conversion processes for clean liquid biofuel production

Process and gas phase modelling

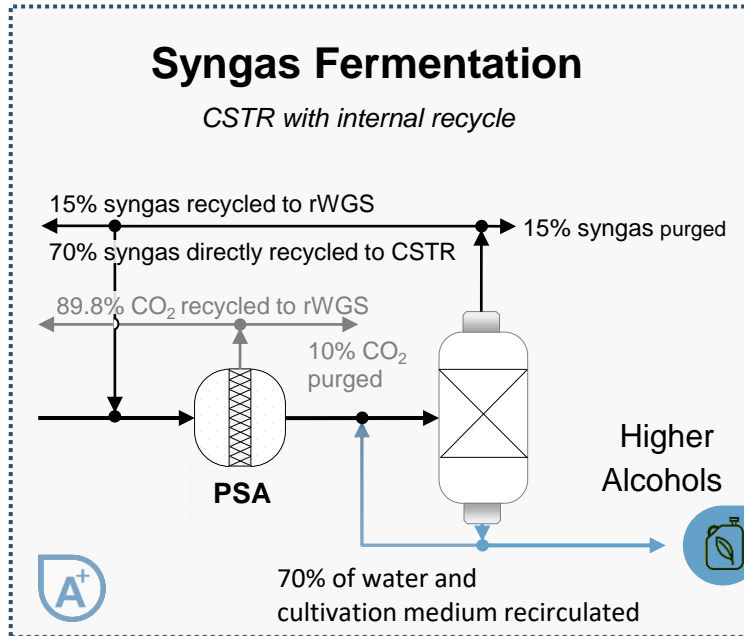
→ Integrated process option





Syngas fermentation model

Process modelling



Reactor conditions

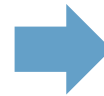
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$T = \text{const} = 37 \text{ }^\circ\text{C}$

$\text{pH} = \text{const} = 6$

$\tau_l = 8 \text{ h}, \tau_g = 1 \text{ h}$

For $V_R = 4800 \text{ m}^3$: 92% CO conversion



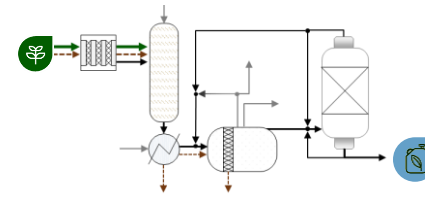
Large-scale fermentation:

CSTRs in industry: up to 300 m³

Spec. power input 2 kW_{el}/m³

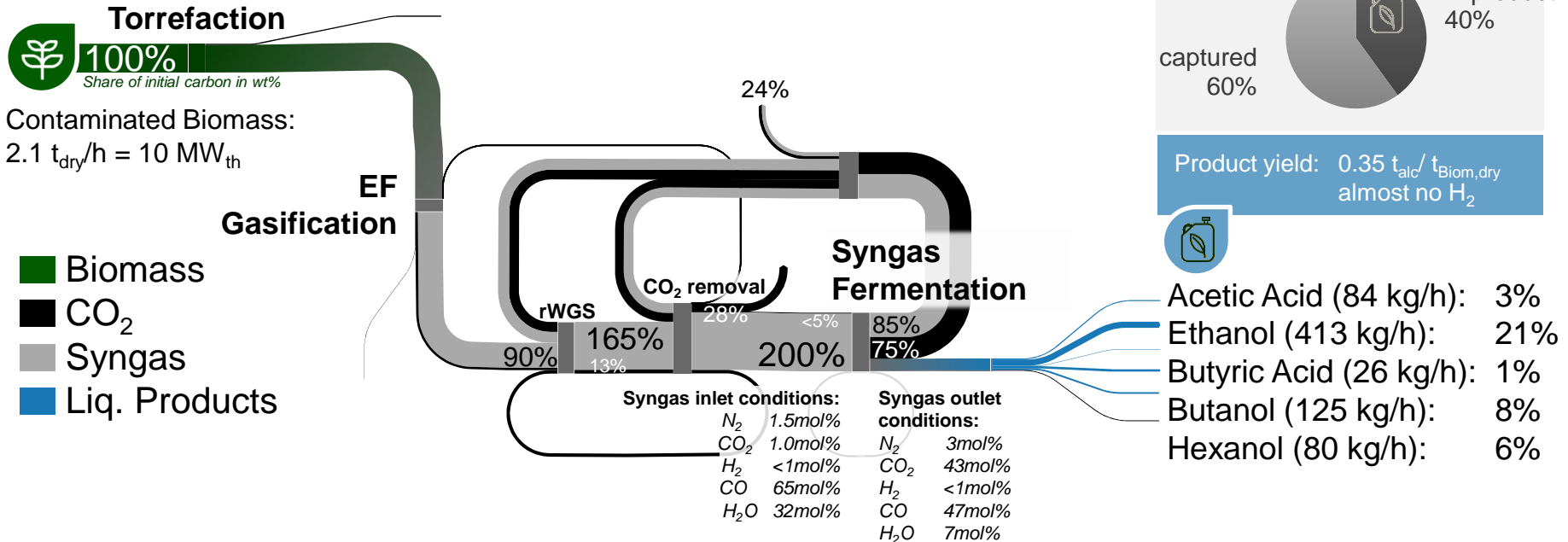
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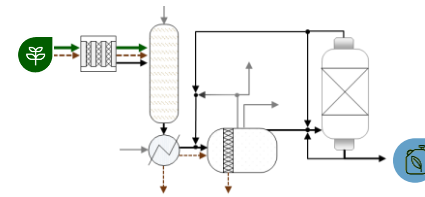
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Process and gas phase modelling

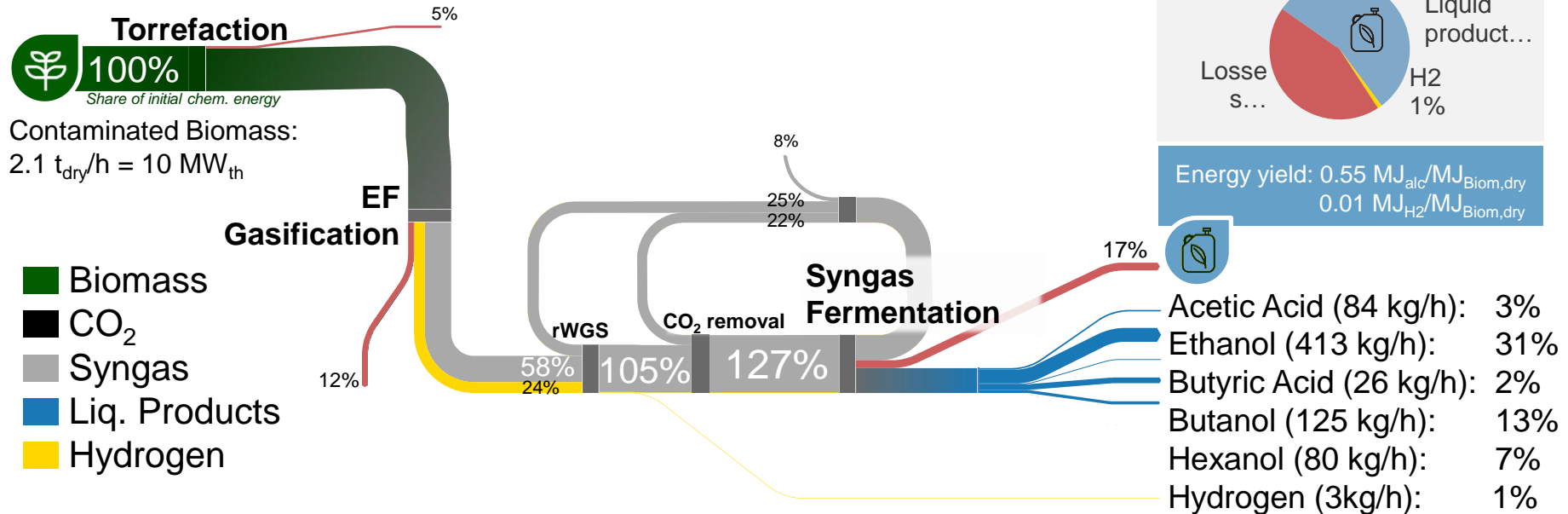
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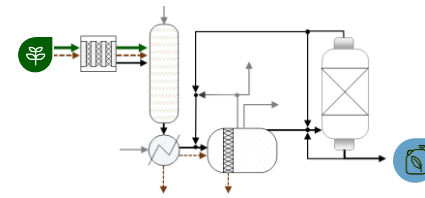




Process and gas phase modelling

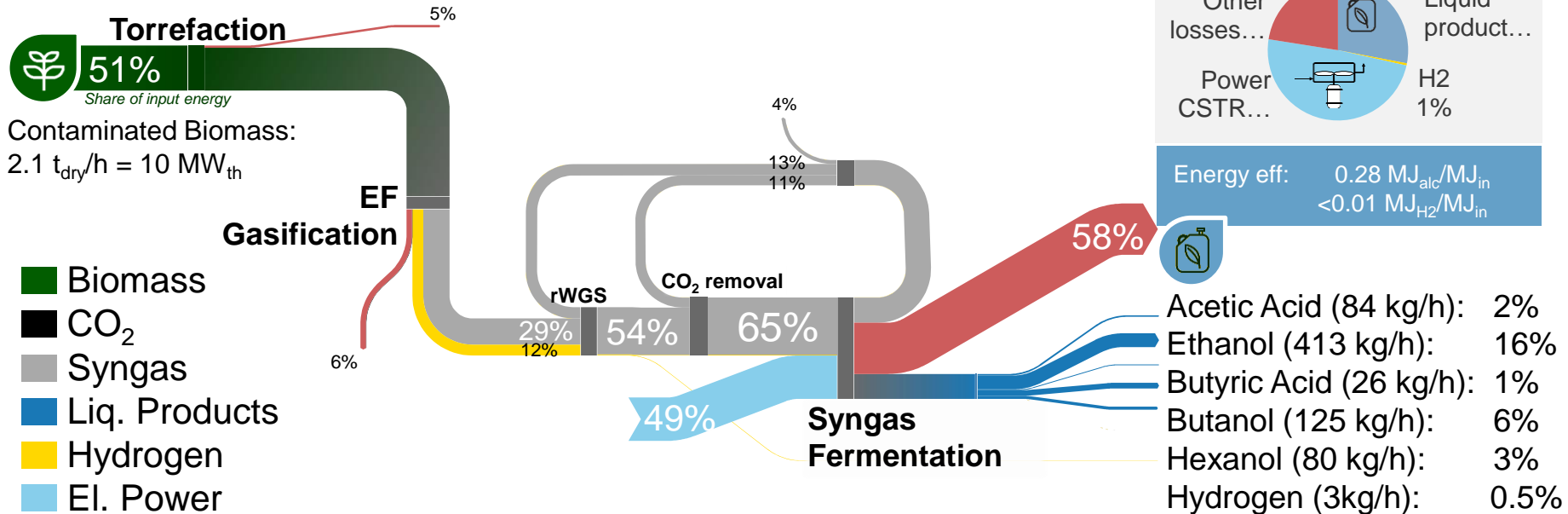
Energy flow diagram and energy efficiency





Process and gas phase modelling

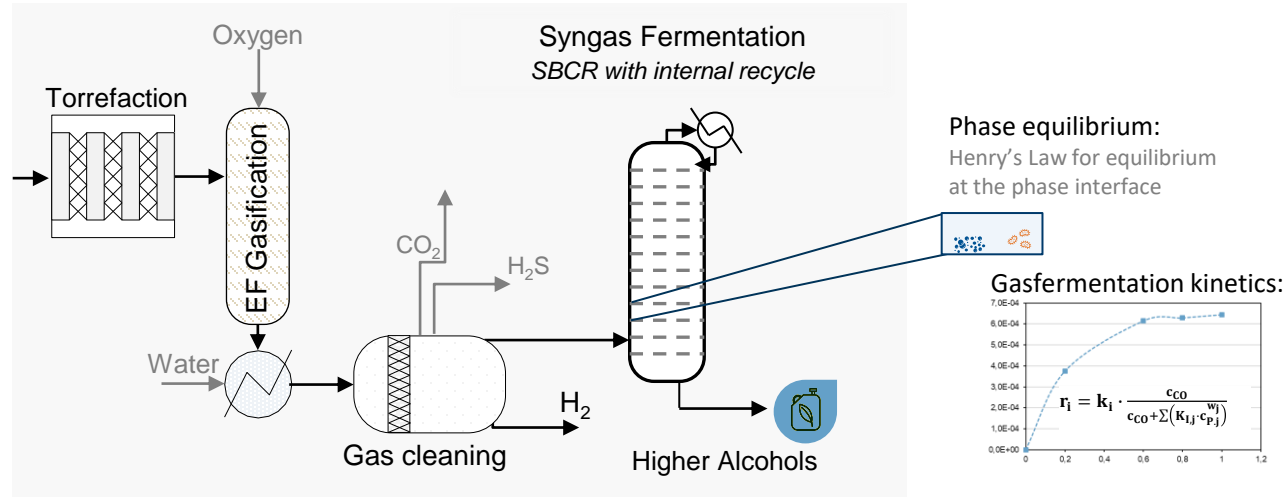
Energy flow diagram and energy efficiency



Conversion processes for clean liquid biofuel production

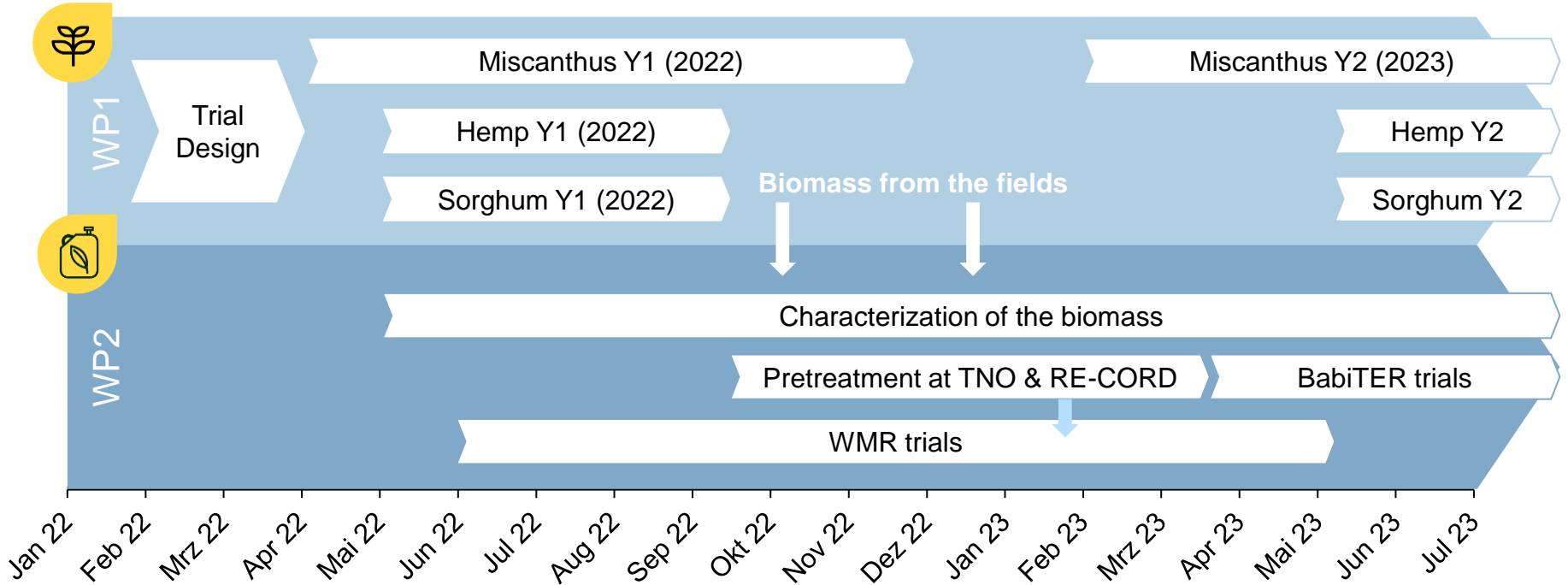
Outlook

Process using bubble column reactor



- low pressure drop
- excellent heat transfer rates per unit volume reactor
 → better temperature control
- higher effective interfacial areas
- little maintenance required due to simple construction
 → relatively cheap to construct and operate

Timeline and Outlook

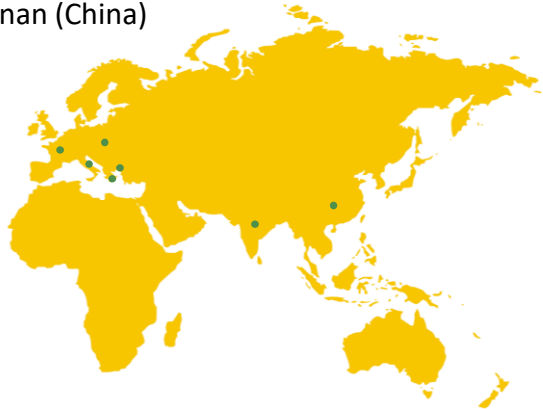


Optimization of energy crops for phytoremediation purposes

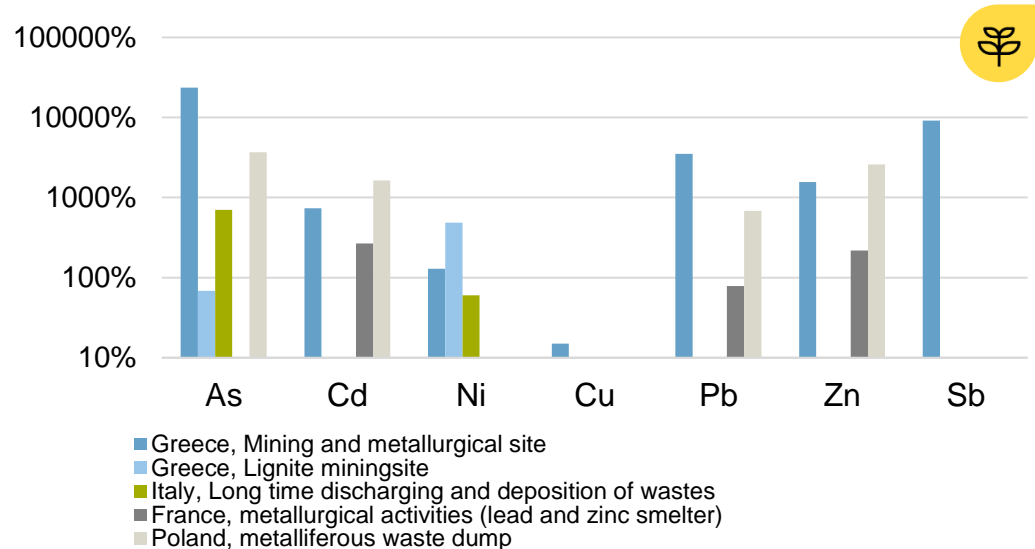
Experimental results 2021

Field trials at seven sites:

- Metaleurop Nord (France)
- Bologna (Italy)
- Silesia (Poland)
- Lavreotiki and Kozani (Greece)
- New Delhi (India)
- Hunan (China)



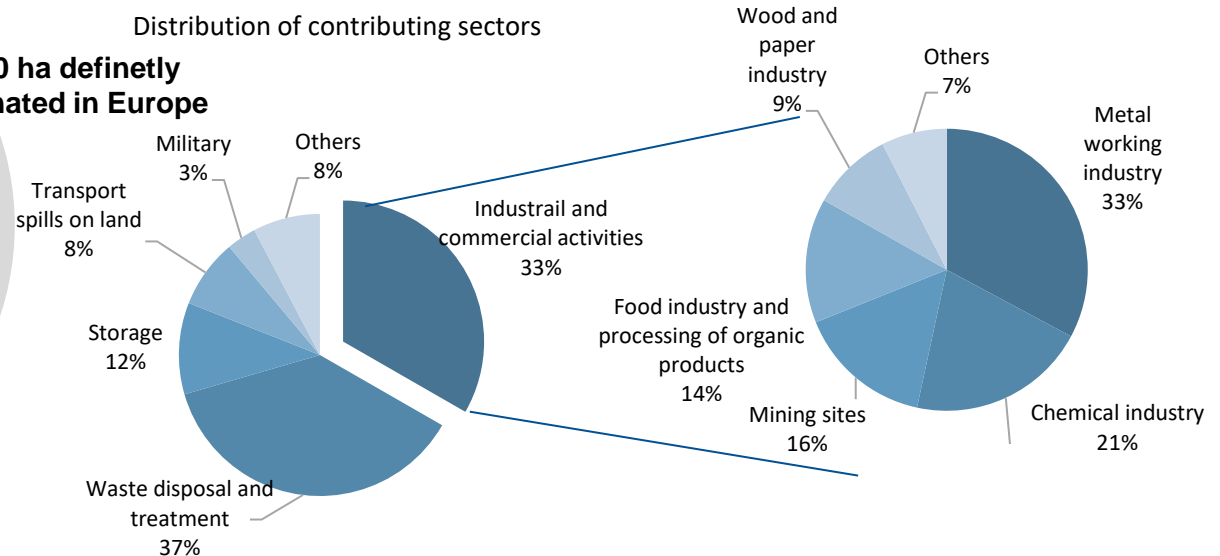
Soil contamination at field sites compared to normal concentrations



Motivation and Project Idea

Contaminated soils and phytoremediation

Soil pollution is one of the greatest concerns among the threats to soil resources in Europe and globally.



Bridging the gap between phytoremediation solutions on **G**rowing energy **c**rops on contaminated **L**an**D**s and clean biofuel production

Highlights

- Growing selected high-yielding lignocellulosic energy crops on contaminated lands with dual scope; the biomass production and the soil remediation.
- Producing clean liquid biofuels with low ILUC risks and collection of the contaminants in a concentrated form.
- Two conversion routes will be developed: **a) entrained flow gasification and syngas fermentation** and b) autothermal pyrolysis and FT synthesis to fuels.
- Developing and modelling optimized phytoremediation strategies for soil decontamination and setting the base to return them back to agriculture.
- Setting up and **modelling optimised value chains** in terms of cost and sustainability towards the sustainable development goals (SDGs).
- Promoting International collaboration on biofuels and more specifically the Innovation Challenge 4 advanced on biofuels with the participation of three leading and highly consuming countries (Canada, China, and India)

State of the Art

Contaminated soils and phytoremediation

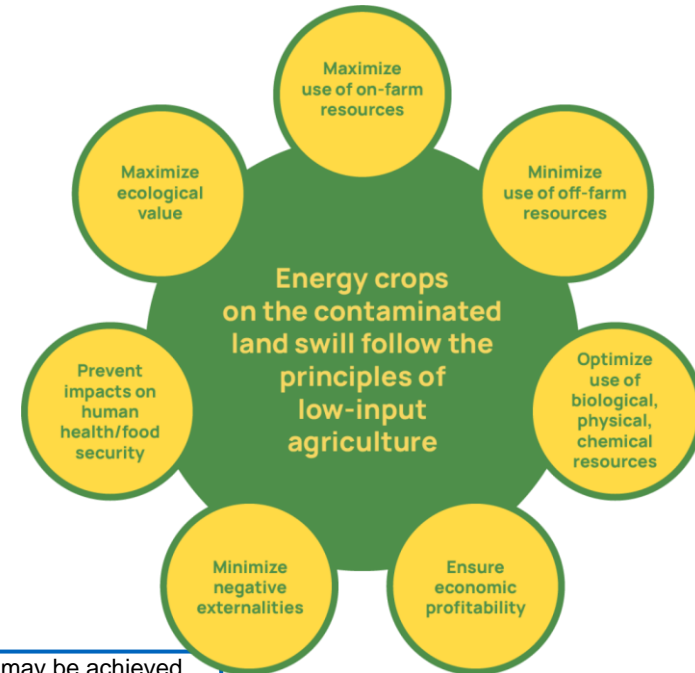
Use of plants to remove contaminants from soil or to render them harmless.

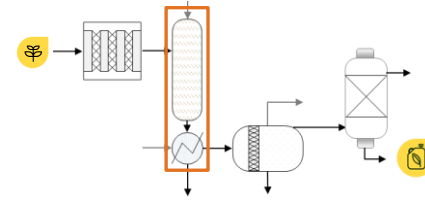
- relatively cheap,
- non-invasive and
- publicly acceptable technology that
- improves the physical, chemical, and biological quality of contaminated soils.
- demonstration and pilot projects have been translated into commercial-scale operations

Phytoremediation is more effective and economically viable when:

- it is applied in large areas with low to medium concentrations of pollutants so that phytotoxicity on plant remains low and plants can grow,
- the crops used produce high addedvalue biomass providing a revenue,
- the site is in unused/abandoned arable land and agricultural practices and mechanization can be applied.

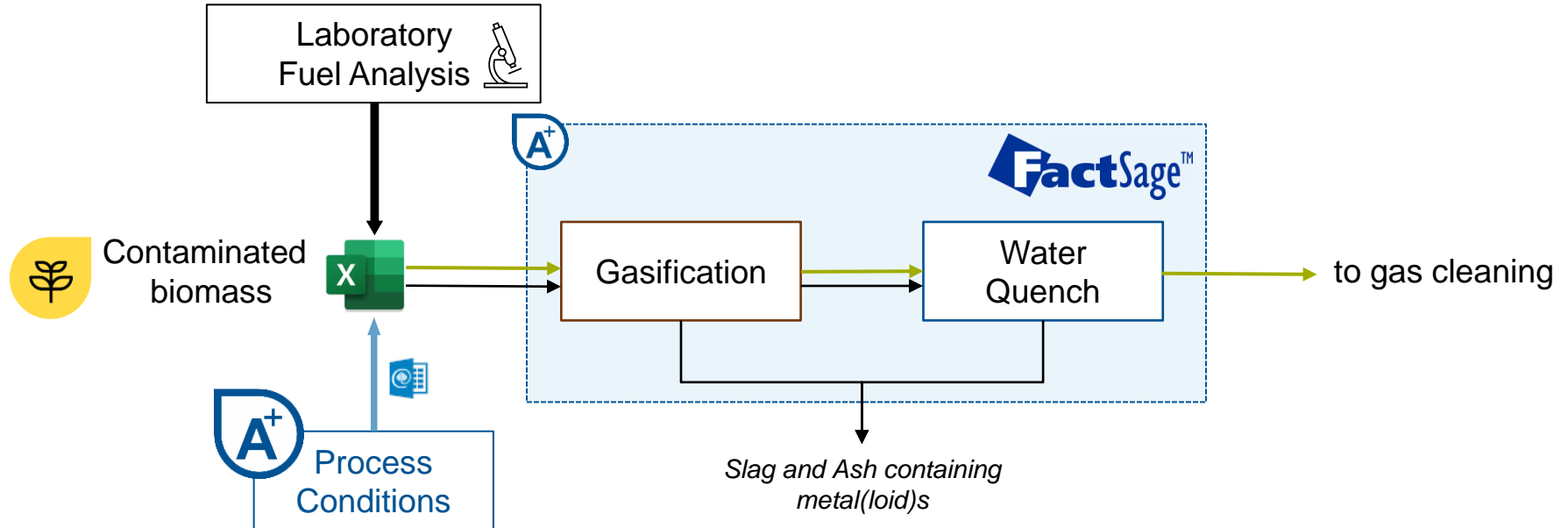
Combining phytoremediation with the production of biomass with a high economic value => a double target may be achieved. harvested biomass can be used as feedstock for bioenergy purposes, and concurrently, plants are decontaminating the soil. marginal or degraded soils that cannot be given over for food production will be exploited and upgraded, the energy targets of RED II will be supported, new jobs will be created, local farmers will have the possibility to maintain and/or increase their income, and the development of rural areas will be reinforced.

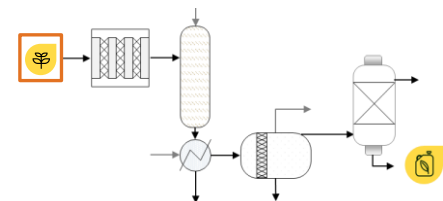




Conversion processes for clean liquid biofuel production

Methodology: Process and gas phase modelling



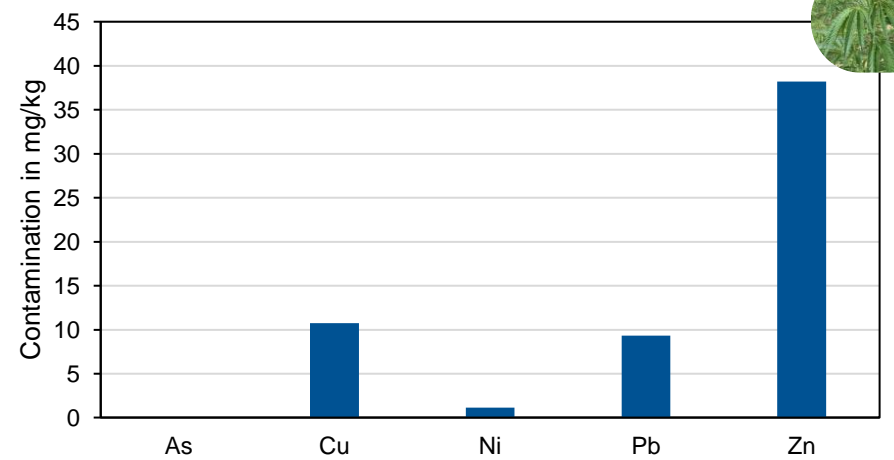


Process and gas phase modelling

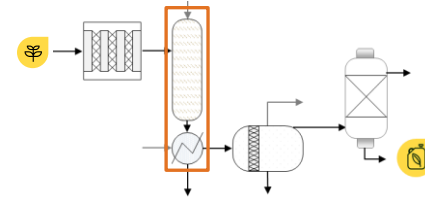
Laboratory Fuel Analysis

(Heavy metal) contamination

ICP-OES results for contaminated hemp



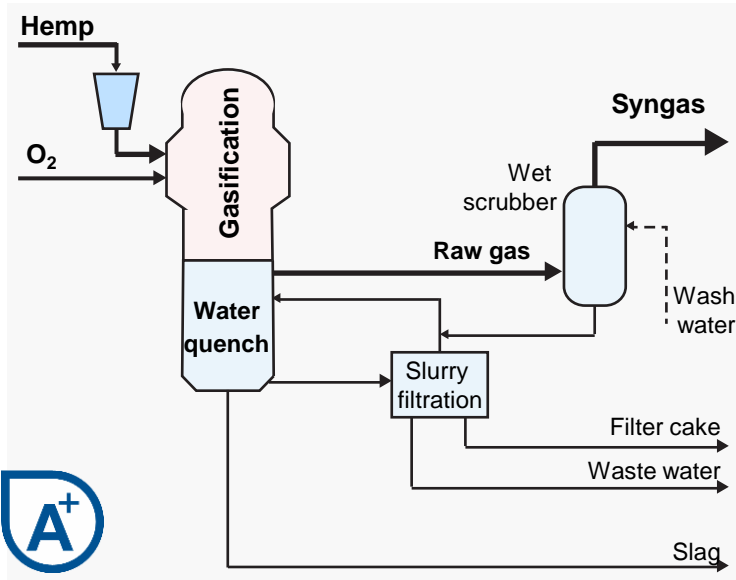
Proximate analysis				
		ar	dry	daf
H2O	wt%	6.57	-	-
Volatiles	wt%	71.04	76.04	82.62
Ash	wt%	7.45	7.97	-
Fixed-C	wt%	14.94	15.99	17.38
Ultimate analysis				
C	wt%	45.20	48.38	52.57
H	wt%	4.68	5.00	5.44
N	wt%	1.10	1.18	1.28
S	wt%	0.14	0.15	0.16
O	wt%	34.68	37.12	40.33
Cl	wt%	0.19	0.20	0.22
HHV/LHV analysis according to DIN 51900-1				
		ar	dry	daf
HHV	kJ/kg	17424.50	18649.79	20264.82
LHV	kJ/kg	16236.42	17378.16	18883.07
Ash melting temperatures				
		Deformation hemisphere		Flow
550°C Imaging Carbon standard		1337	1528.6	1585



Process and gas phase modelling

Aspen Plus Gasification Model

Syngas production in O₂-blown entrained flow gasification



- Pressurized EFG (30 bar) with direct full water quench
- Decomposition through thermally coupled reactor: Non-conventional solids → conventional solids
- NH₃ + HCN formation:

f_N according to literature

$$X_{NH_3} = \frac{27}{17} \frac{1 - f_N}{f_N} X_{HCN} = \frac{1}{2} X_{N_2} = \left[3 + \frac{17}{27} \frac{f_N}{1 - f_N} \right]^{-1}$$

- Restricted thermodynamic equilibrium approach
Mean gasification temperature set via oxygen supply

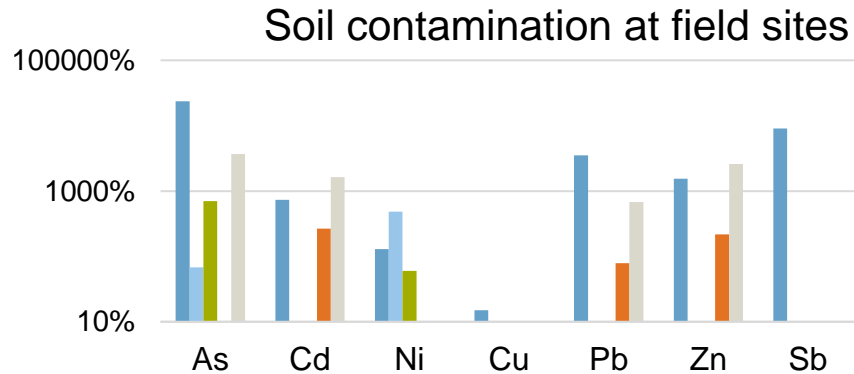


λ as result and input for gas phase modelling

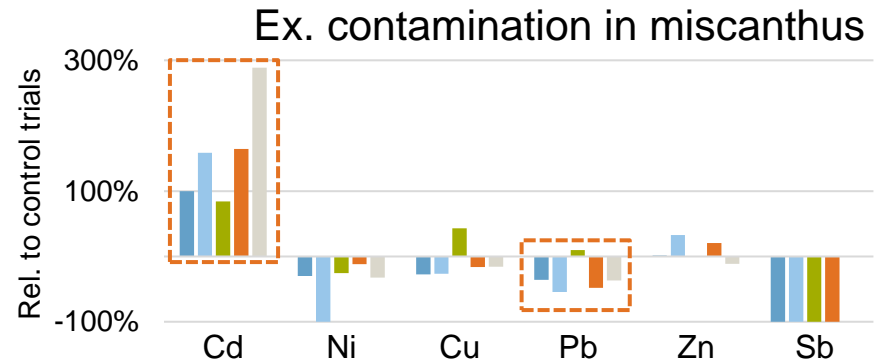
Optimization of energy crops for phytoremediation purposes

Results 2021

Partners with field experiments and pot trials



- Greece, Mining and metallurgical site
- Greece, Lignite miningsite
- Italy, Long time discharging and deposition of wastes
- France, metallurgical activities (lead and zinc smelter)
- Poland, metalliferous waste dump

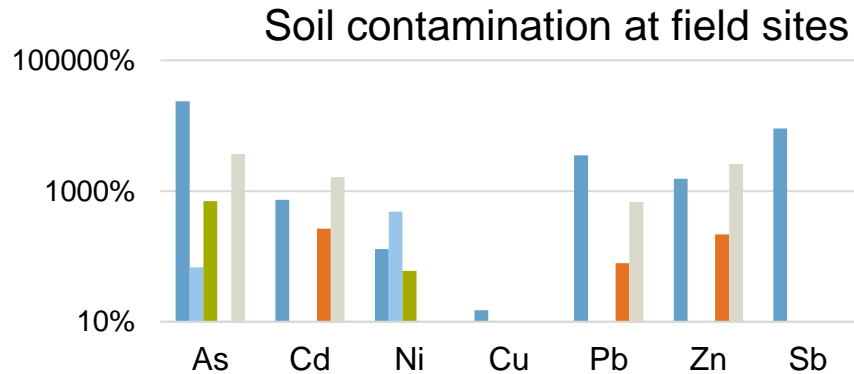


- Lonite
- Mycorrhiza
- Lonite+Mycorrhiza
- Siapton
- Siapton + Mycorrhiza

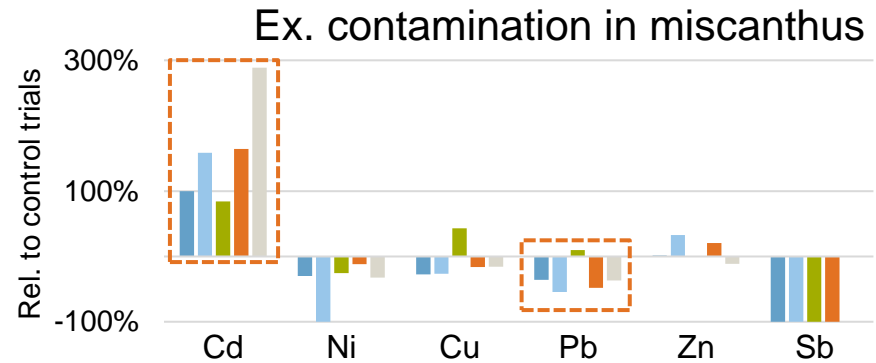
Optimization of energy crops for phytoremediation purposes

Results 2021

Partners with field experiments and pot trials



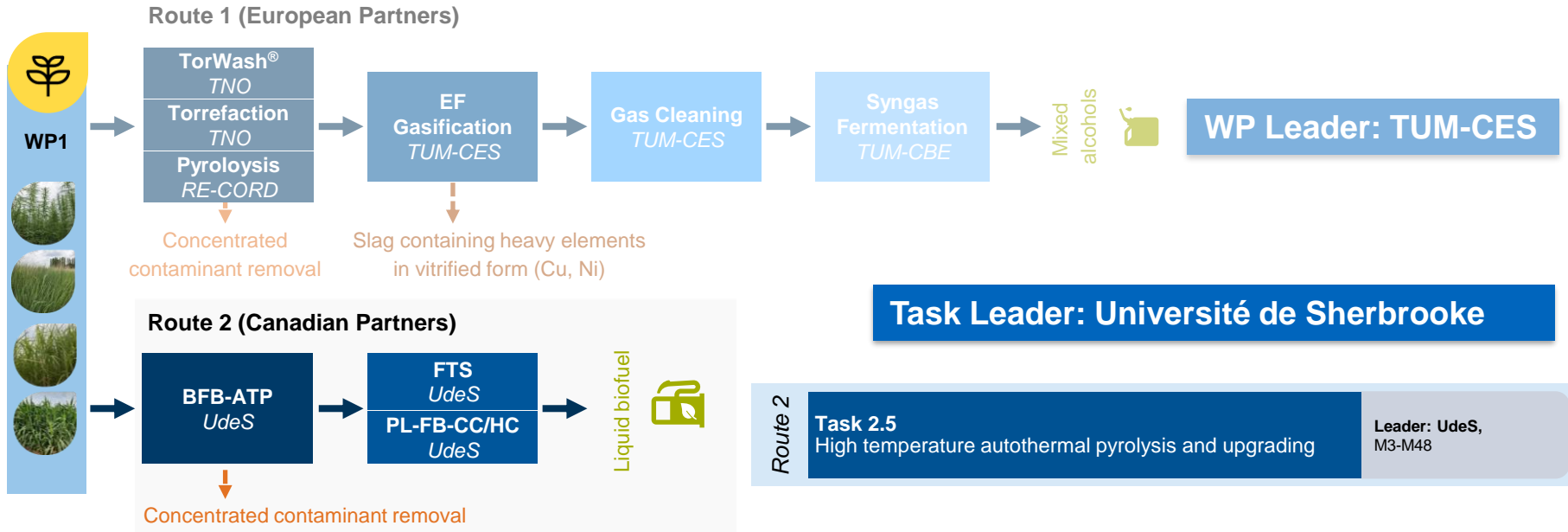
- Greece, Mining and metallurgical site
- Greece, Lignite miningsite
- Italy, Long time discharging and deposition of wastes
- France, metallurgical activities (lead and zinc smelter)
- Poland, metalliferous waste dump



- Lonite
- Mycorrhiza
- Lonite+Mycorrhiza
- Siapton
- Siapton + Mycorrhiza

Conversion processes for clean liquid biofuel production

Process routes to be investigated: Route 2



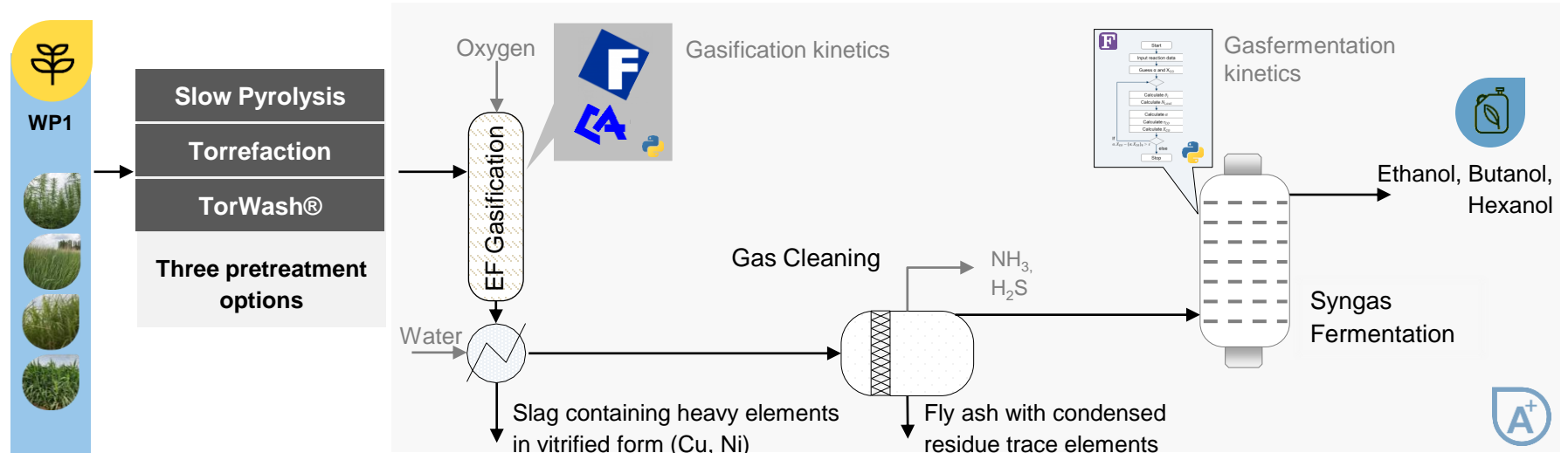
Conversion processes for clean liquid biofuel production

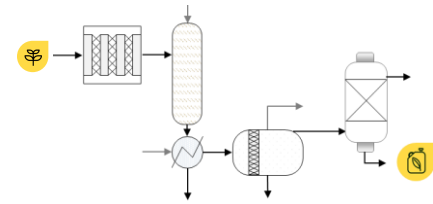
Process and gas phase modelling

Task 2.1.3
Process and gas phase modelling

Leader: CERTH,
partners: TUM
M1-M48

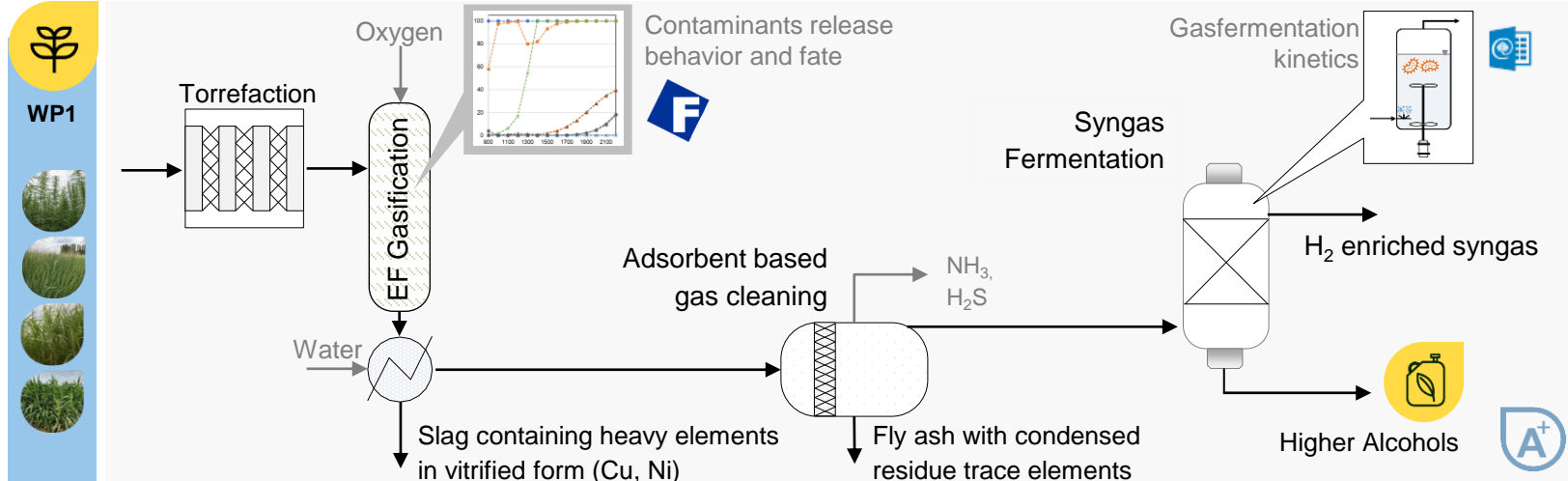
Year 1				Year 2				Year 3				Year 4																																			
2021				2022				2023				2024				2025																															
M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A												
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48





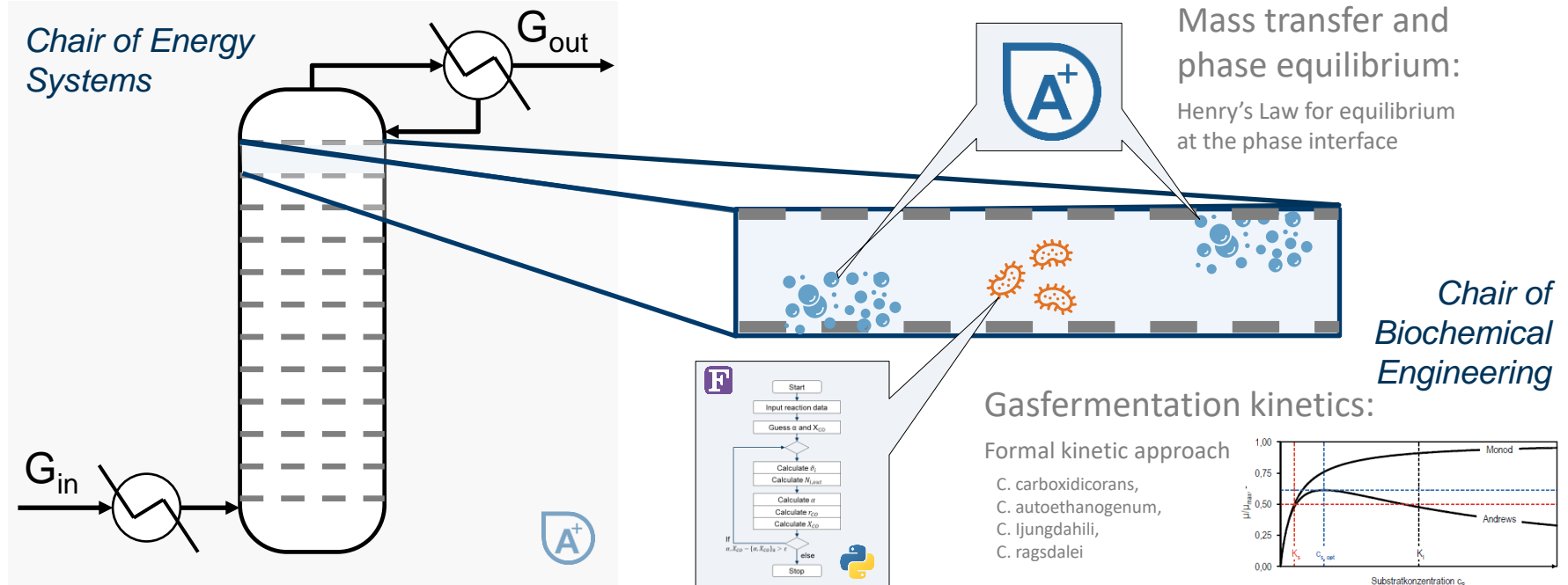
Process and gas phase modelling

Process scaling and overview



Syngas fermentation

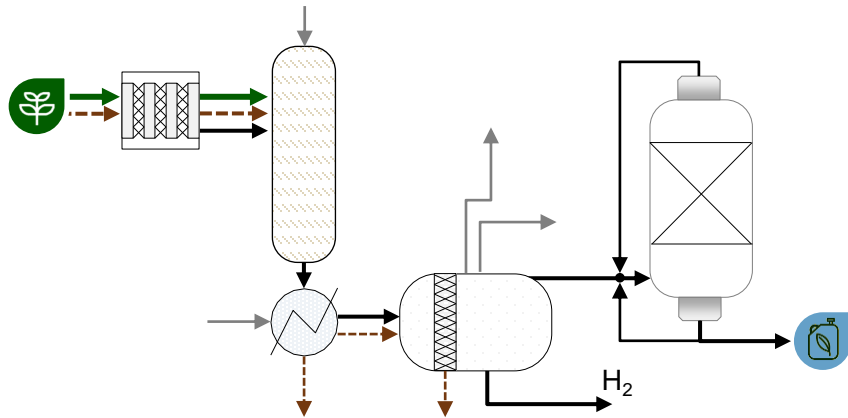
Modelling Approach: Bubble Column Reactor



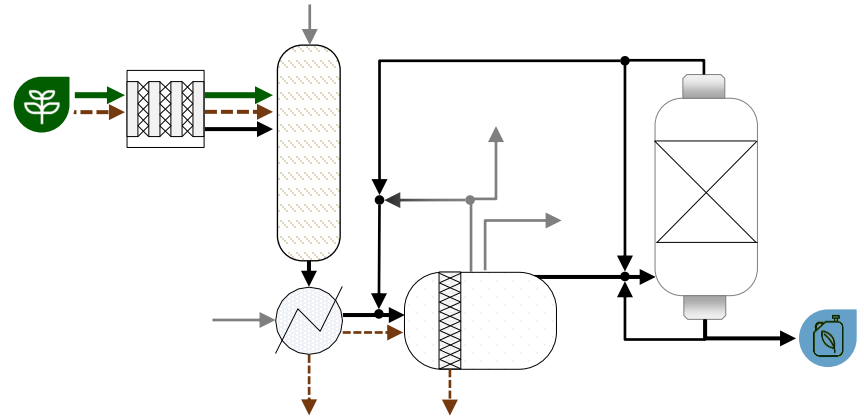
Conversion processes for clean liquid biofuel production

Summary

“Once-through” process

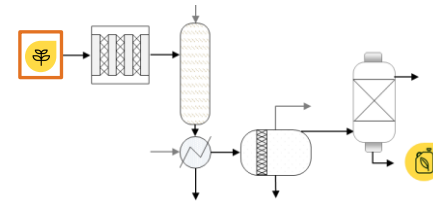


Integrated process



Grenzwerte laut Düngemittelverordnung

Nebenbestandteil	Kennzeichnung ab ... mg/kg TM	Toleranz in % des gekennzeichneten Wertes jeweils bis zu	Grenzwert mg/kg TM
Magnesium (Mg)	0,1 %	50 %, 1 %-Punkt	
Kupfer	0,05 %	20 %, 0,4 %-Punkt	
Zink	0,1 %	20 %, 0,4 %-Punkt	
Selen (Se)	0,0005 %	25%	
Kobalt	0,004 %	20 %, 0,4 %-Punkt	
Basisch wirksame Bestandteile (als CaO)	5%	50 %, 2,5 %-Punkte	
Arsen (As)	20	50%	40
Blei (Pb)	100	50%	150
Cadmium (Cd)	1,0	50%	1,5
Cadmium (Cd) für Düngemittel ab 5 % P₂O₅ (FM)	20 mg/kg P ₂ O ₅		50 mg/kg P ₂ O ₅
Chrom (ges.)	300	50%	–
Chrom (Cr^{VI})	1,2	50%	2
Nickel (Ni)	40	50%	80
Quecksilber (Hg)	0,5	50%	1,0
Thallium (Tl)	0,5	50%	1,0



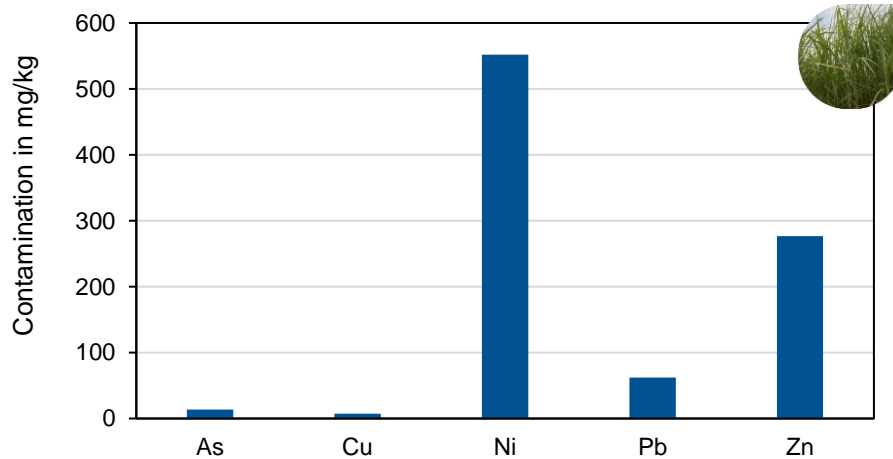
Process and gas phase modelling

Laboratory Fuel Analysis

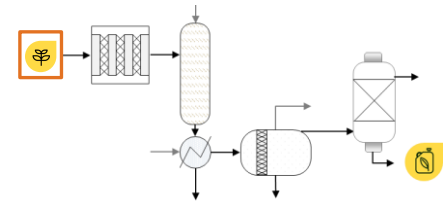
(Heavy metal) contamination



ICP-OES results for contaminated sorghum



Fuel test report				
Proximate analysis				
		ar	dry	daf
H2O	wt%	5.12	-	-
Volatiles	wt%	69.56	73.31	78.91
Ash	wt%	6.74	7.10	-
Fixed-C	wt%	18.59	19.59	21.09
Ultimate analysis				
C	wt%	38.17	40.23	43.30
H	wt%	5.77	6.08	6.54
N	wt%	1.15	1.21	1.31
S	wt%	0.19	0.20	0.22
O	wt%	41.43	43.66	47.00
Cl	wt%	1.45	1.52	1.64
HHV/LHV analysis according to DIN 51900-1				
		ar	dry	daf
HHV	kJ/kg	16806.00	17711.97	19065.38
LHV	kJ/kg	15413.89	16244.81	17486.12
Ash Melting Temperature in °C				
		Deformation	hemisphere	Flow
550°C Imaging Carbon st.		898	1202.7	1235

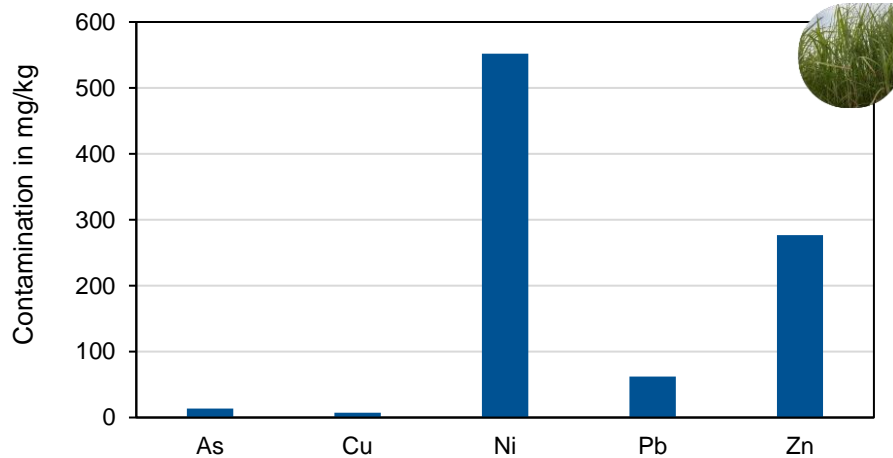


Process and gas phase modelling

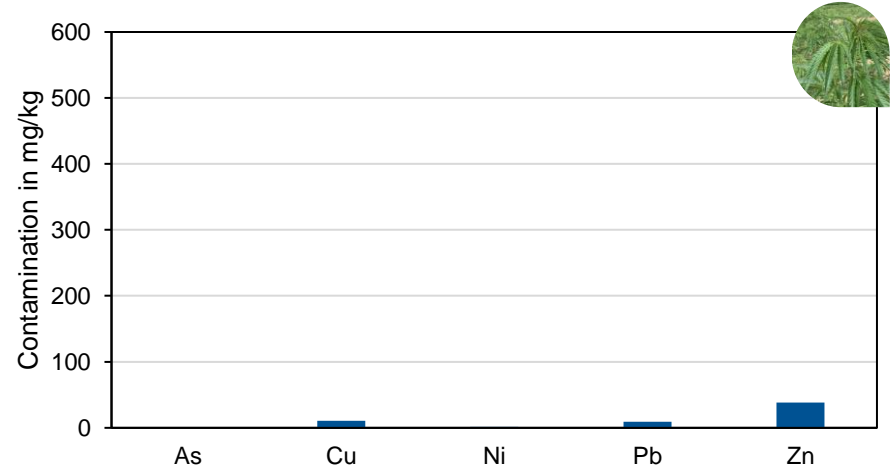
Laboratory Fuel Analysis

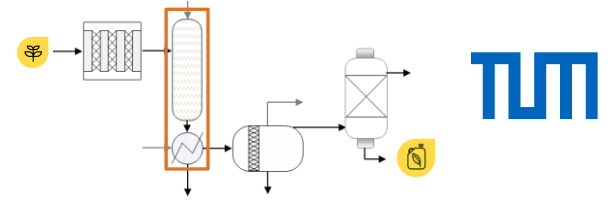
(Heavy metal) contamination 

ICP-OES results for contaminated sorghum



ICP-OES results for contaminated hemp



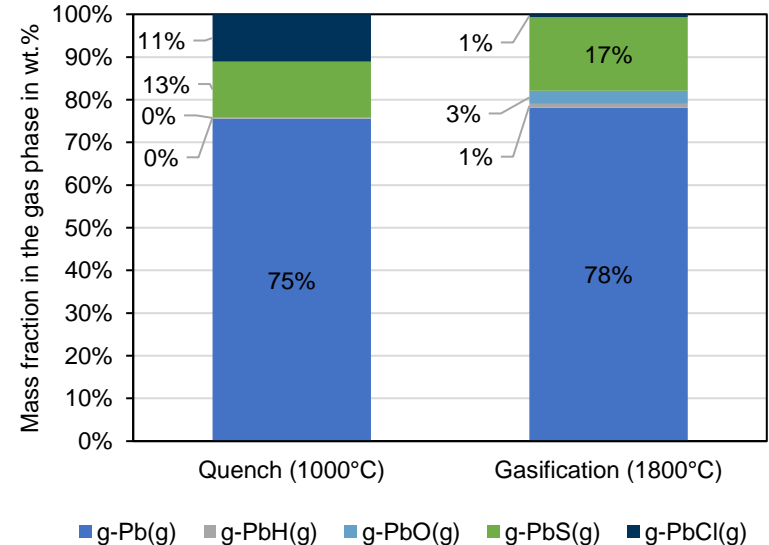
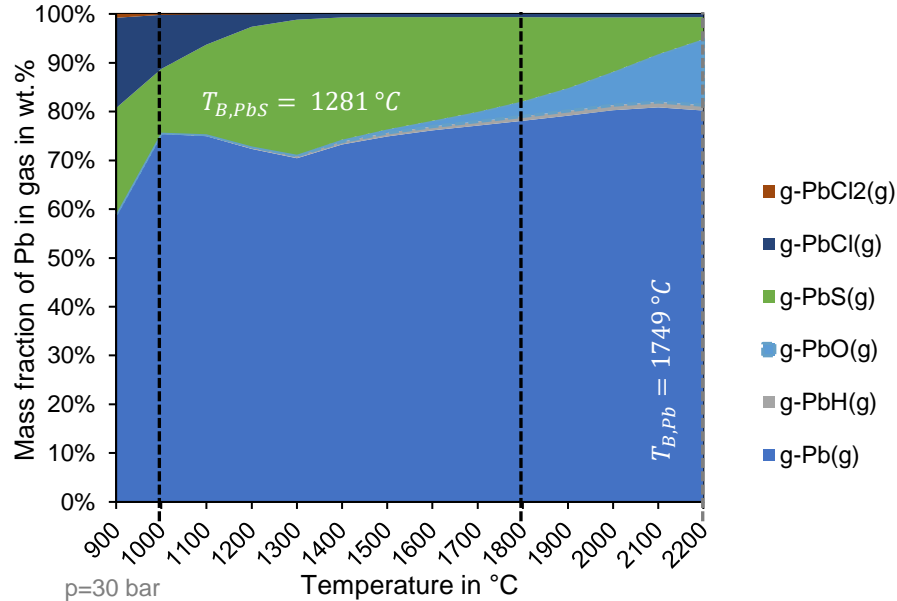


Gas phase modelling

Preliminary FactSage Gasification Model

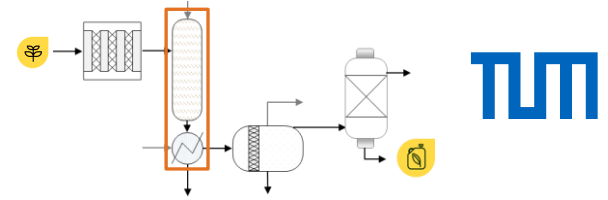


Mass Distribution of Pb in gas phase

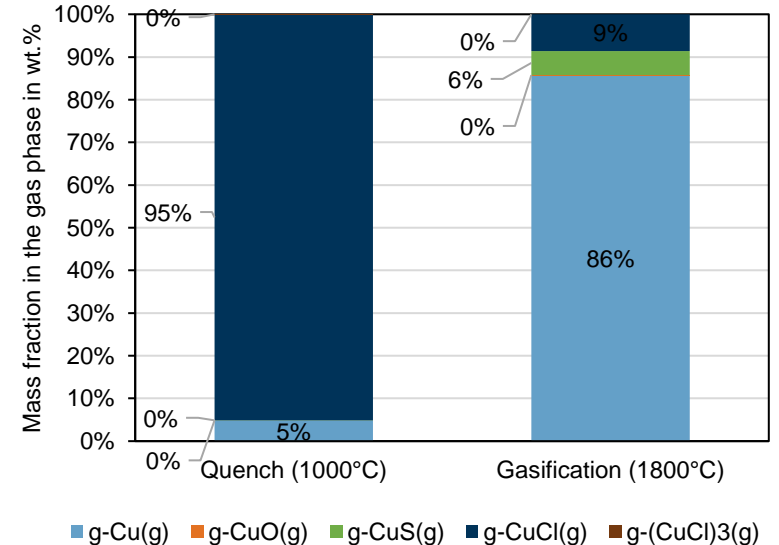
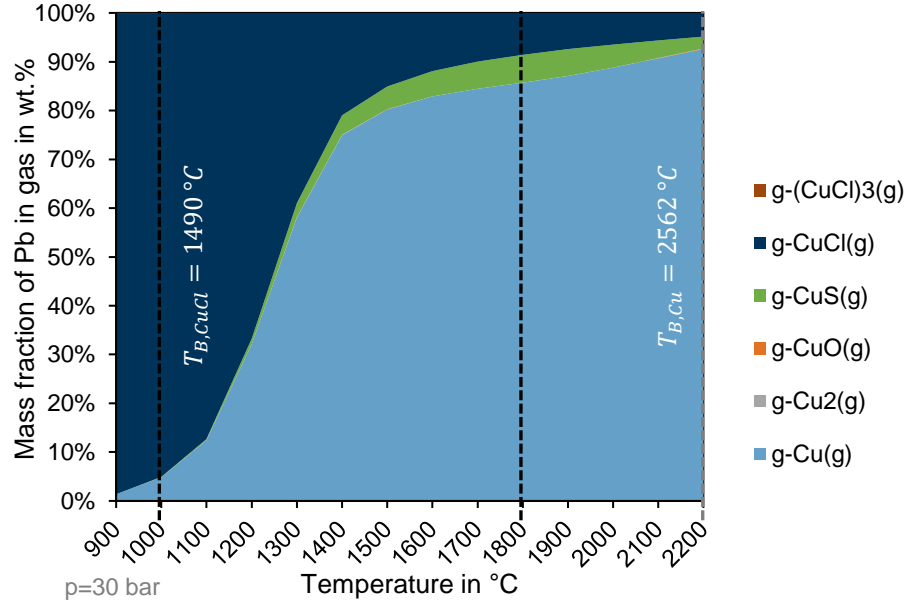


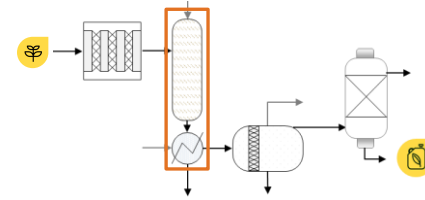
Gas phase modelling

Preliminary FactSage Gasification Model



Mass Distribution of Cu in gas phase



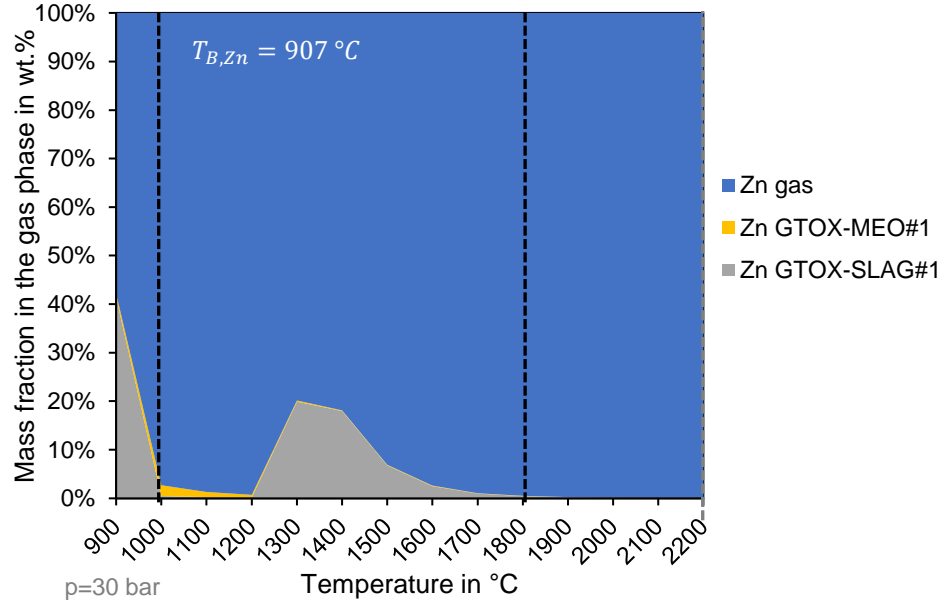


Gas phase modelling

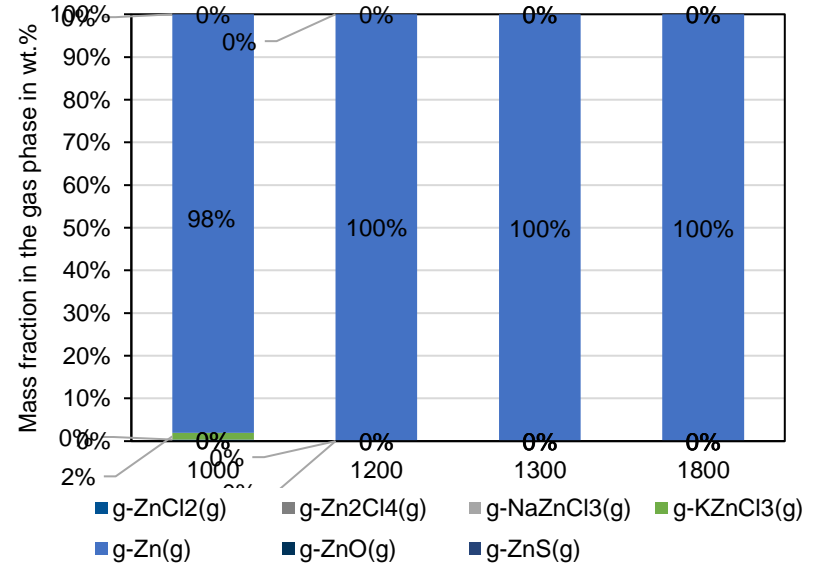
Preliminary FactSage Gasification Model



Mass Distribution of Zn



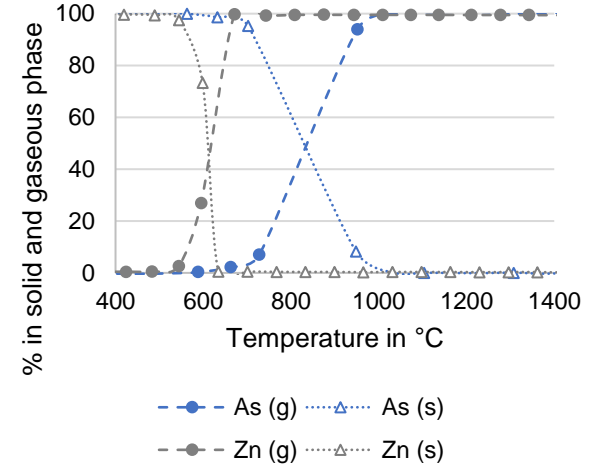
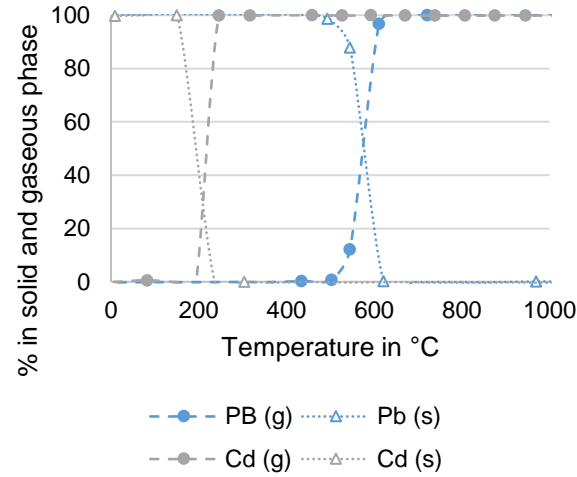
Mass Distribution of Zn in gas phase



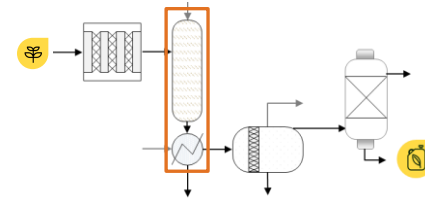
Conversion processes for clean liquid biofuel production

Process and gas phase modelling

	GOLD	Jiang et al.
Al		238.34
As		0.33
Cd	1.4	0.39
Co		0.25
Cr		4.59
Cu	7.06	11.09
Fe		656
Hg		0.017
Mg		2205.2
Mn		39.86
Ni	3.63	0.97
Pb	34.53	2.21
Zn	162.34	45.82

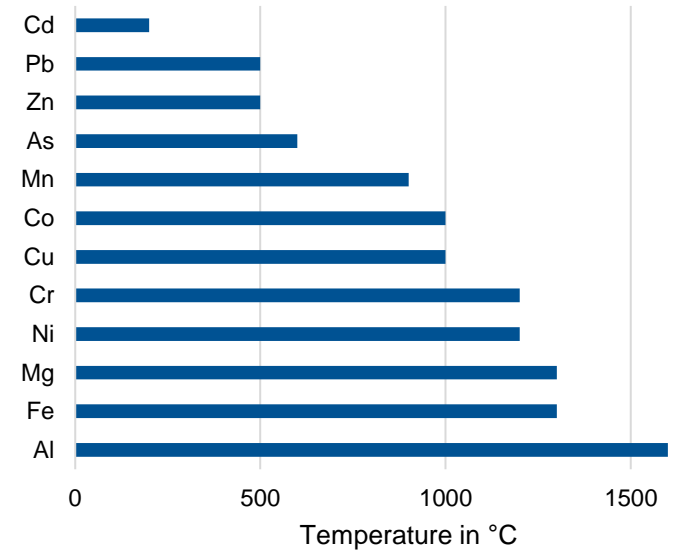
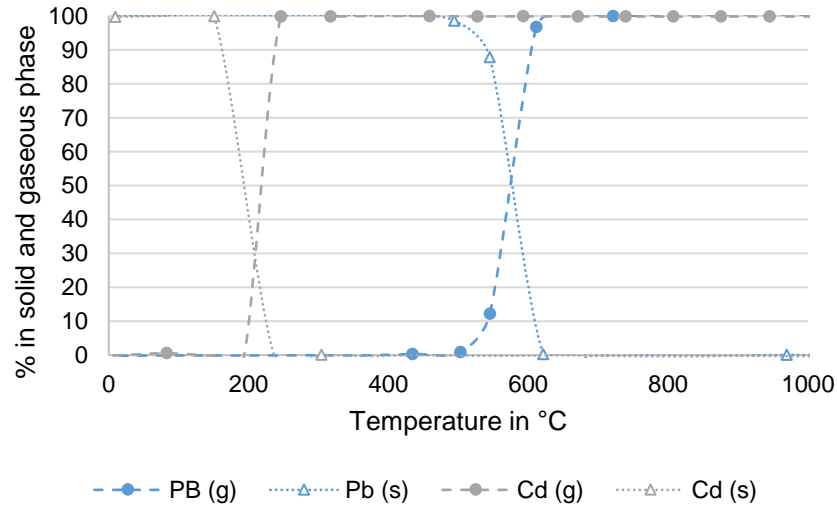


Jiang et al. 2016: Solid–gaseous phase transformation of elemental contaminants during the gasification of biomass. In Sc. Ott Env.



Gas phase modelling

FactSage modelling



Jiang et al. 2016: Solid–gaseous phase transformation of elemental contaminants during the gasification of biomass. In Sc. Ott Env.

Wire Mesh Reactors

Wire mesh reactor for high temperatures (WMR-HT) and with optical ports (WMR-OP)

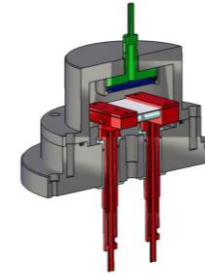
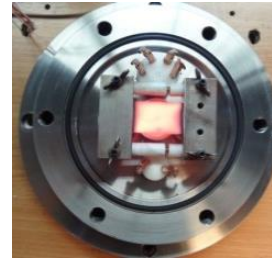
Test rig data:

- Temperature: up to 1800 °C
(WMR-HT)
- Temperature: up to 1200 °C
(WMR-OP)
- Pressure range: atm to 5.0 MPa
(WMR-HT)
- Pressure range: atm to 2.0 MPa
(WMR-OP)
- Heating rate: > 1000 K/s
- Atmosphere: N₂, Ar, O₂, CO₂

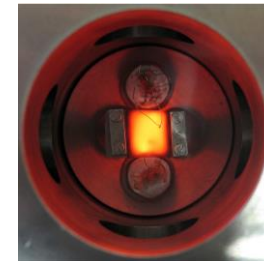
Research focus:

- Devolatilization kinetics of solid fuels
- Reaction kinetics of solid fuel gasification

WMR-HT:



WMR-OP:



BabiTER (Baby High Temperature Entrained Flow Reactor)

Atmospheric entrained flow gasification

Test rig data:

- Temperature: up to 1600 °C
- Pressure: atmospheric
- Residence time: up to 2 s
- Dosing system: vibrating chutes
- Fuel input: two independent units,
each 50-300 g/h
- Atmosphere: N_2 , O_2 , H_2O , CO_2 , H_2 , CO

Research focus:

- Investigation of pyrolysis and gasification
- Determination of gasification kinetics
- Investigation of co-gasification
- Analysis of char structure
- Analysis of product gas composition
- Accessible for in-situ optical measurement



Biomass Pilot-Scale Entr. Flow Gasifier (BOOSTER)

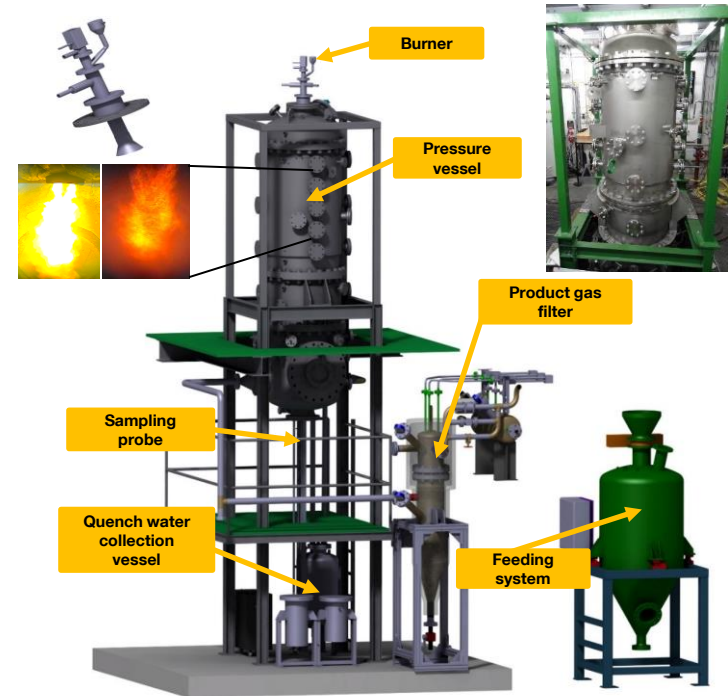
Autothermal biomass gasification (100kW)

Test rig data:

- Operation: autothermal
- Temperature: up to 1500°C
- Pressure: 0 to 5 barg
- Fuel input: 100 kW (+/- 25 %)
- Dosing system: pneumatic
- Gasif. media: Air, O₂, H₂O, CO₂
- Operation time: ~10 h

Research focus:

- Industry-like design (realistic conditions)
- Investigation of cold gas efficiency, gas quality, ash melting behavior, tars, ...



Motivation and Project Idea

Phytoremediation and Biofuel Production

Contaminated biomasses as a promising alternative for bioenergy production with a three-fold aim:

1. to produce clean bioenergy and helping to cover global energy demands;
2. to mitigate environmental pollutions through sustainable phytoremediation process; and
3. to avoid the dilemma “food versus biofuel” production

Four high-yielding lignocellulosic energy crops are used:

- miscanthus
- switchgrass
- sorghum and
- industrial hemp



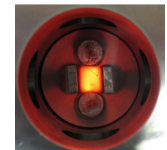
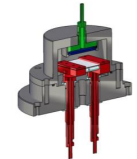
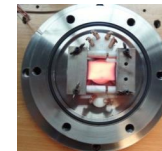
Characterization of biomass

Characterization of biomass and basic experimental gasification characterization

Partner	Description of the analysis
TUM, CErTH, UdeS	<ul style="list-style-type: none"> Proximate analyses (fuels) and loss of ignition of solid samples
TUM, CErTH, UdeS	<ul style="list-style-type: none"> Specific surface area-BET and pore size distribution studies
TUM, CErTH, UdeS	<ul style="list-style-type: none"> Density, porosity, mineralogical and elemental analysis
TUM, CErTH	<ul style="list-style-type: none"> Grain size analysis
TUM, CErTH	<ul style="list-style-type: none"> Cl and F analysis by oxygen bomb combustion/ion selective electrode methods

Experiments on entrained flow reactors, **wire mesh reactors** and thermobalances to analyze:

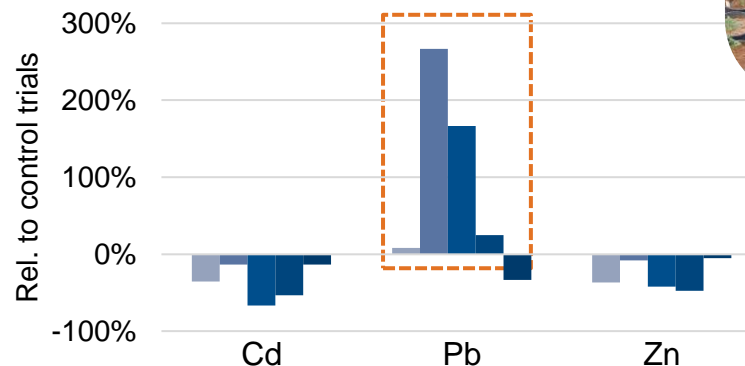
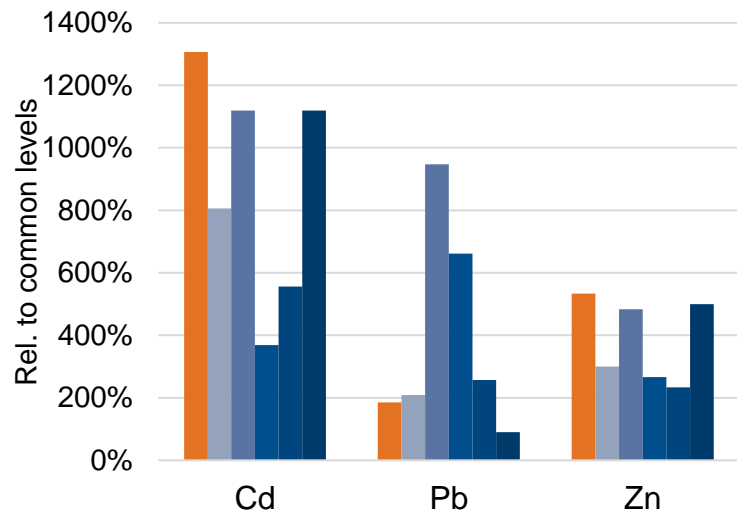
- Reaction kinetics of gasification of feedstock under the EFG conditions,
- Influence of released critical trace substances on subsequent gas purification, e.g. by ICP-OES
- Pretests for investigation of:
 - Grinding behavior and handling ($d_{max} < 250\mu\text{m}$ and $d_{50} \approx 70\mu\text{m}$),
 - Probe preparation (fuel and additive feeding) and
 - Physical and chemical characteristics of treated and untreated fuels.



Optimization of energy crops for phytoremediation purposes

Pot trial results 2021

Exemplarily: contamination in miscanthus in Poland



- Control
- Protein hydrolysates
- Fulvic/humicacids
- Mycorrhiza
- Protein hydrolysates+Mycorrhiza
- Fulvic/humicacids + Mycorrhiza