CERESiS

ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies

Pyrolysis of heavy metals contaminated biomass

Paola Giudicianni
23 April 2024

Contributing partners:
CNR - pyrolysis and combustion, CERTH and NTUA - modelling

Our partners

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This project leading has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101006717

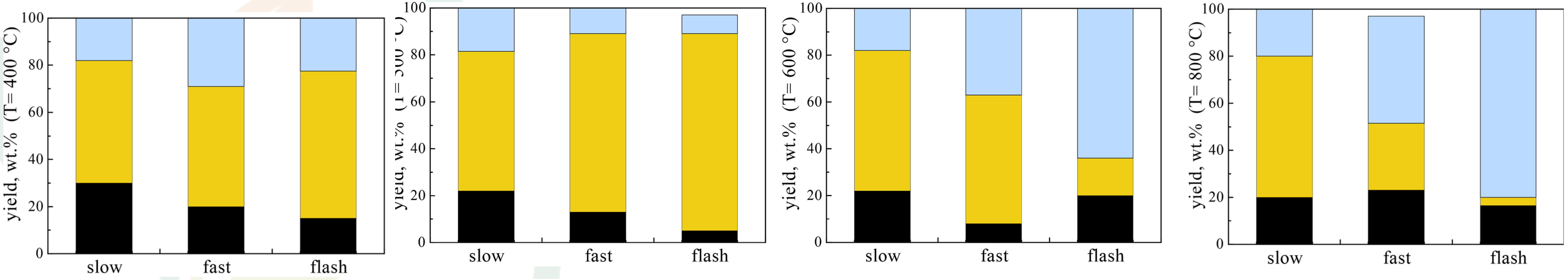
FAPEG Fundação de Amparo à Pesquisa do Estado de Goiás
This project has received funding from the Brazilian Fundação de Amparo à Pesquisa do Estado de Goiás under grant number 202110267000220

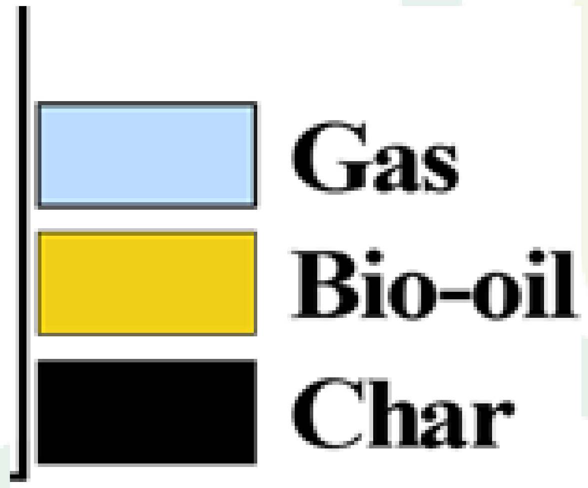
Fonds Nouvelles frontières en recherche / New Frontiers in Research Fund
Fonds de recherche Société et culture Québec
This project has received funding from the Canadian New Frontiers in Research Fund under grant number NFRFG-2020-00148 and the Canadian Fond de recherche Société et culture – Québec under grant number 308509

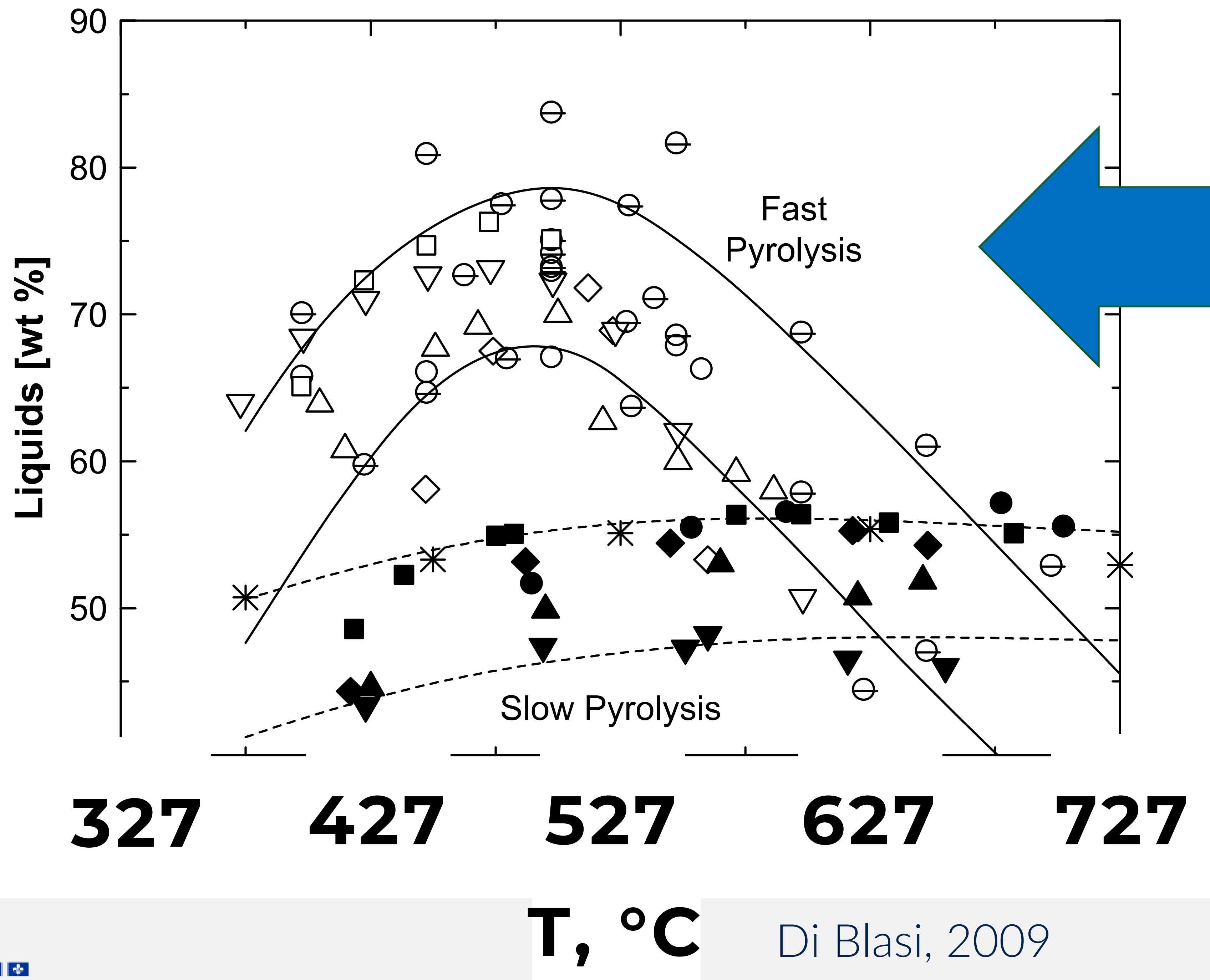
The pyrolysis pathway

SoA of bio-oil production

T=400 °C T=500 °C T=600 °C T=800 °C





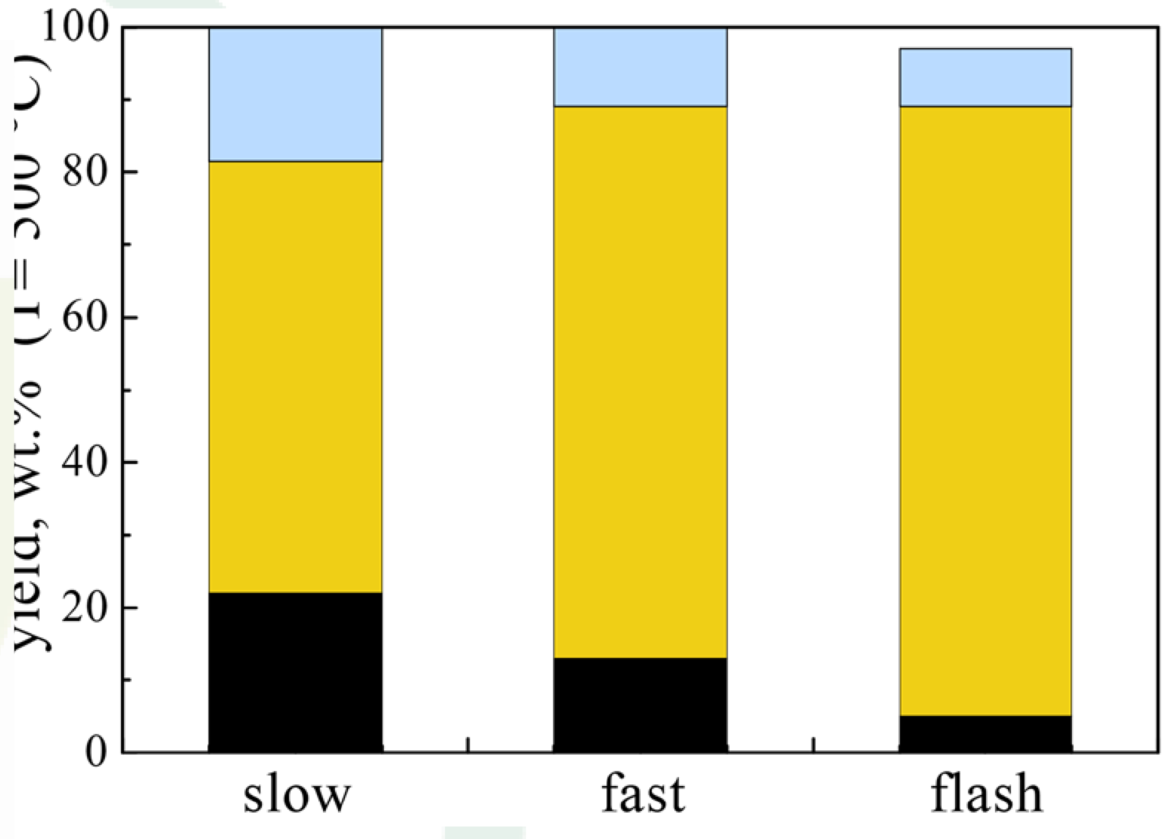


Di Blasi, 2009

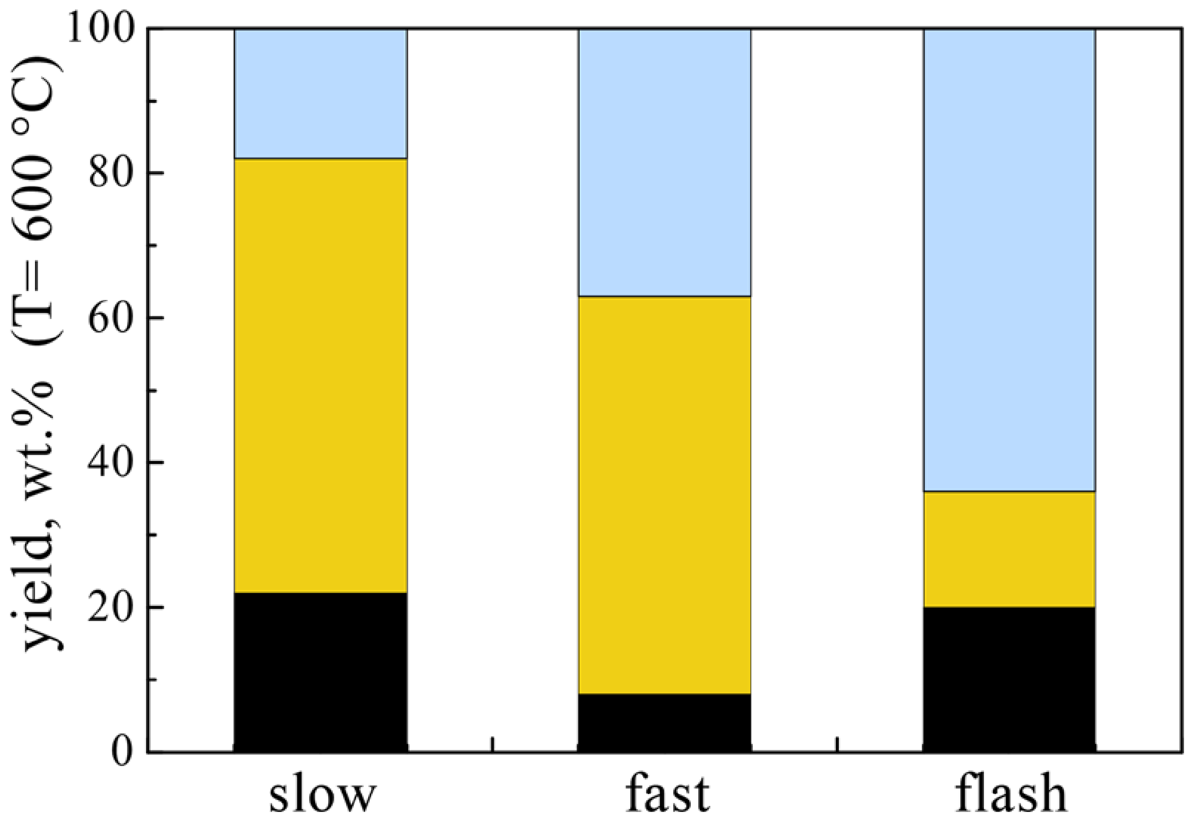
SoA of bio-oil production

T=400 °C

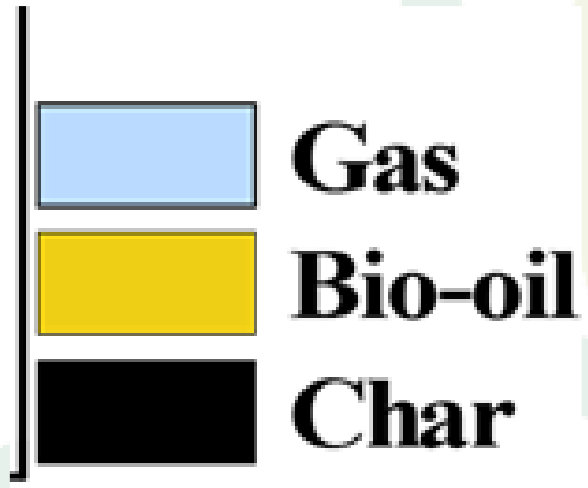
T=500 °C

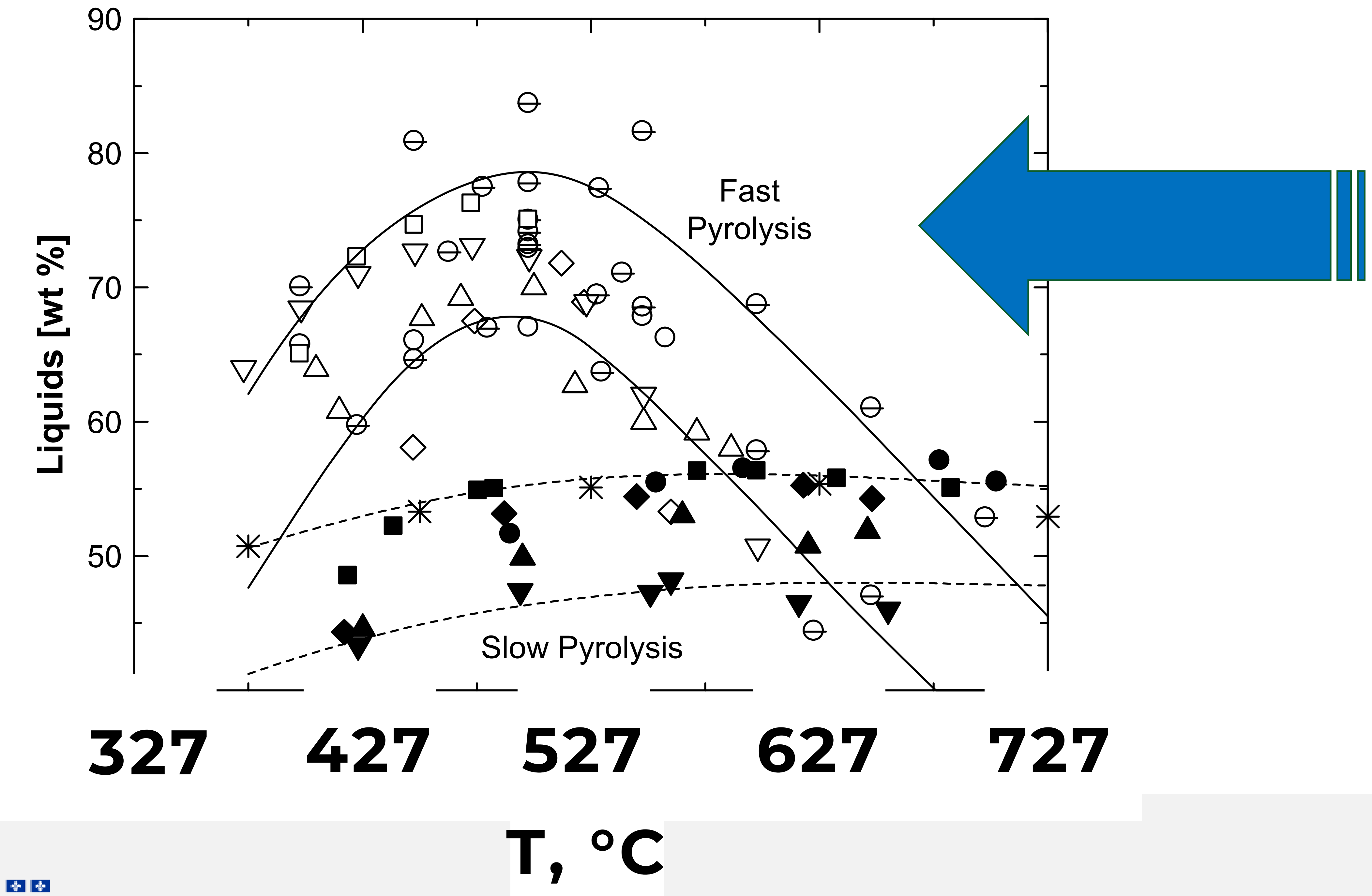


T=600 °C

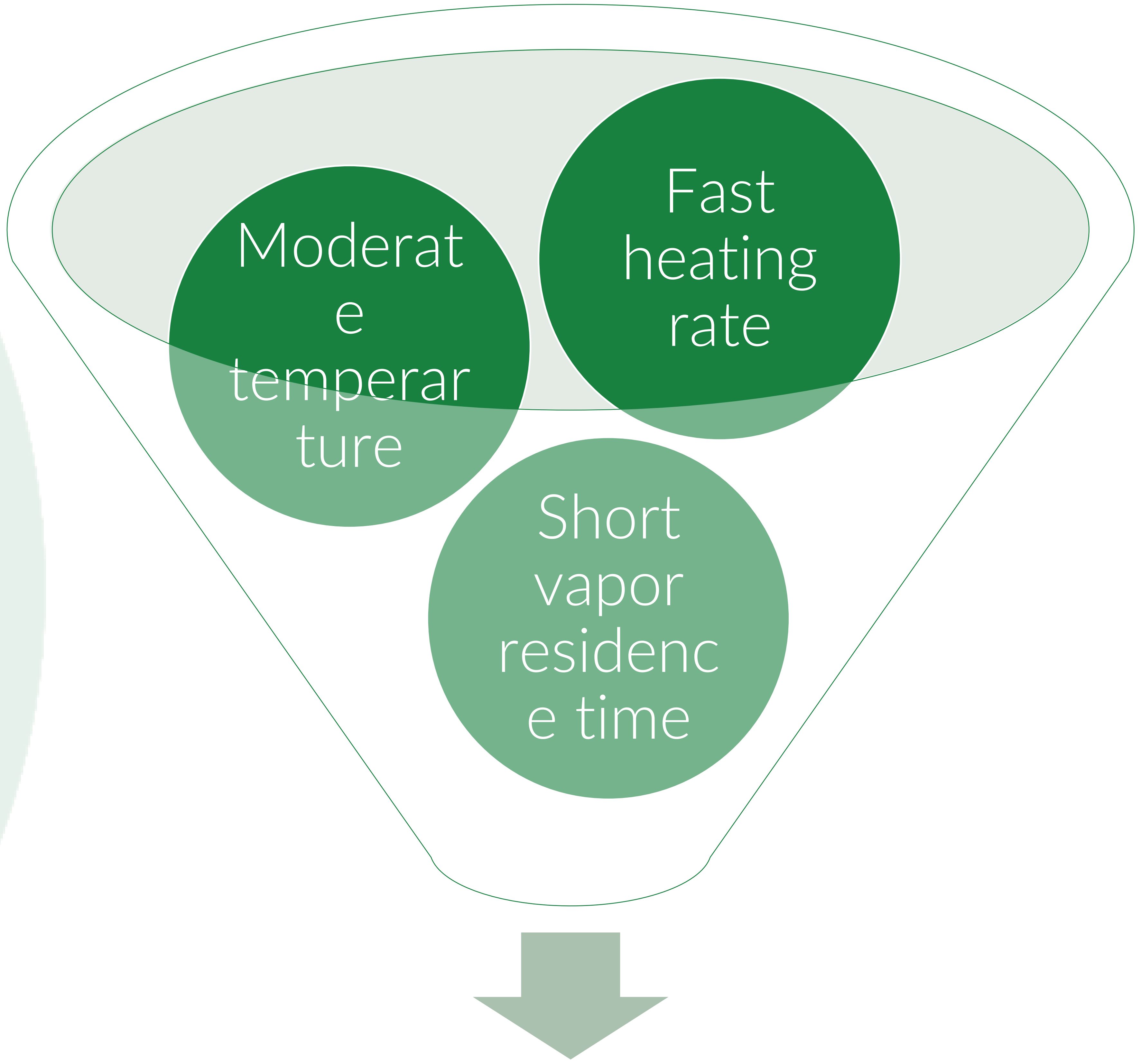


T=800 °C



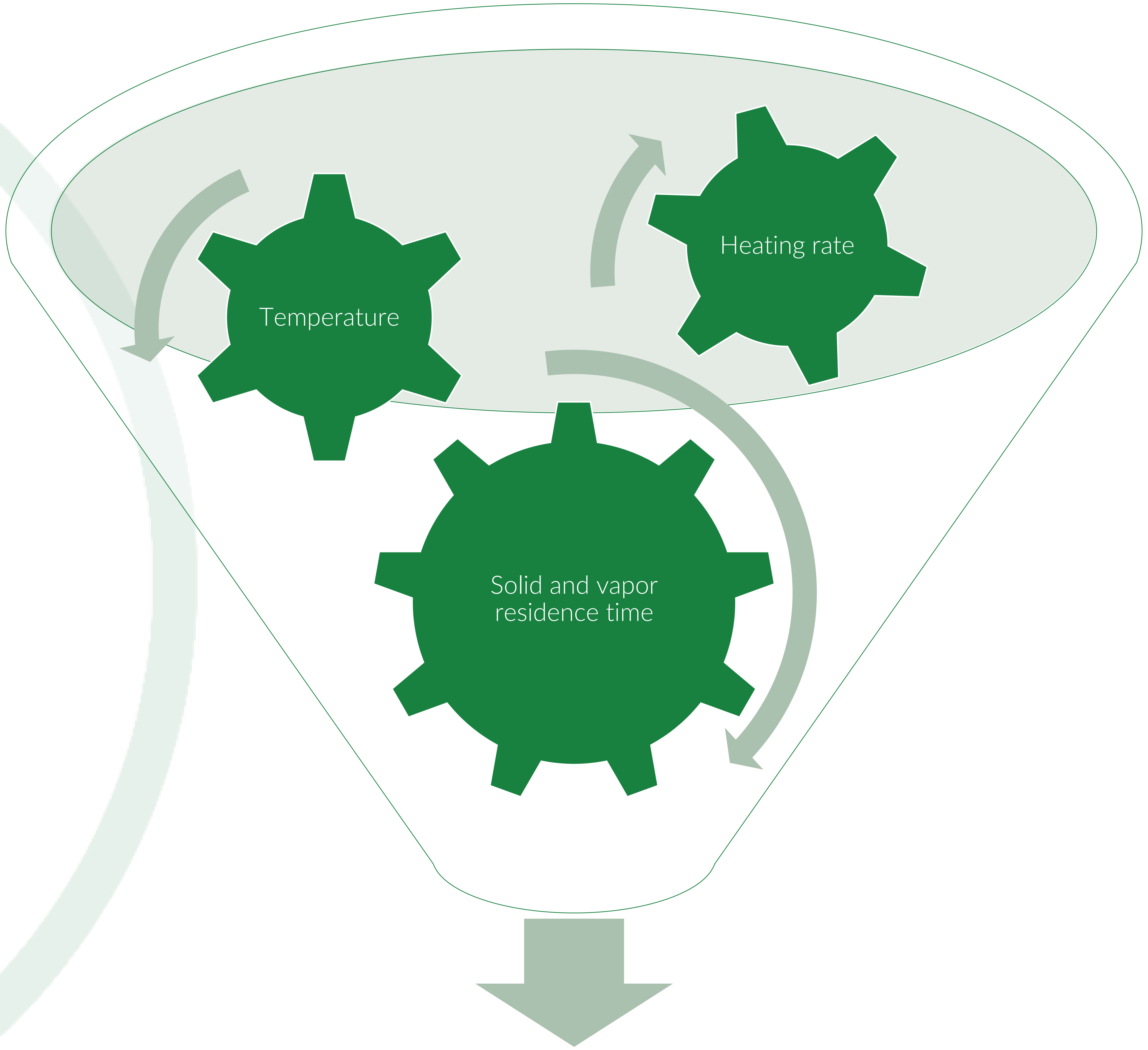


SoA of bio-oil production



High bio-oil yield

Progress beyond SoA



High bio-oil yield

Clean biofuel

Self sustainable pyrolysis

Choice if of the pyrolysis plant configuration

Heating rate

Fast Pyrolysis Plants with Capacity Higher than 10 kg/h in 2020

Company	TRL	Feedstock	Technology
Karlsruhe Institute of Technology/DE	4–5, 6–7	agricultural residues	twin screw reactor
BTG-Btl/NL	4–5, 8	agricultural residues, sludge, animal excrements	rotating cone
Valmet/FI	6–7	forest residues	circulating fluidized bed
Versa Renewables LCC/US	6–7	lignocellulosic biomass	n.a.
Fortum/FI	6–7, 8	forest residues	circulating fluidized bed
Ensyn//CA	6–7, 8	forest residues	circulating transported bed
Red Arrow/US	8	n.a.	circulating transported bed, circulating fluidized bed
Twence/NL	9	forest residues	rotating cone

- Mechanisms for heavy metals displacement from the biomass to the bio-oil
  - Devolatilization
  - Entrainment

High heating rate favors HM devolatilization

- Effect of heating rate of HM devolatilization

Stable combustion becomes more and more challenging

- Reduce gas dilution as much as possible

Choice if of the pyrolysis plant configuration

Heating rate

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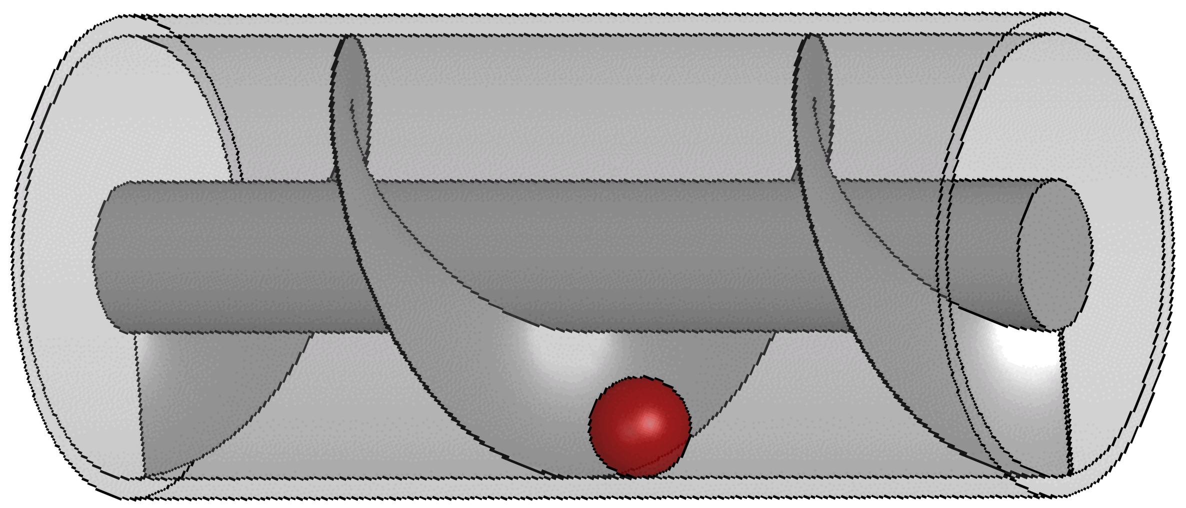
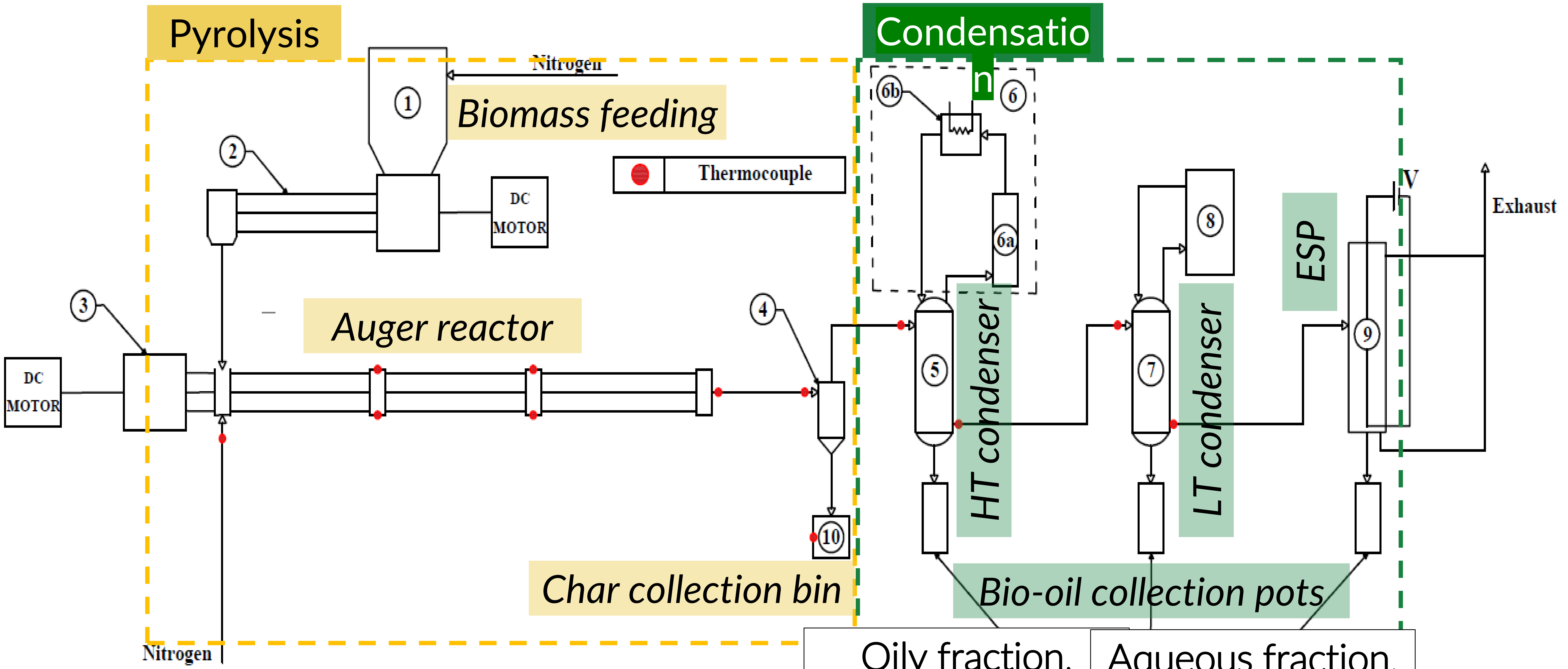
- Proven technology
- Flexible with respect to particle size and composition
- Good control of residence time and temperature
- Good mixing characteristics
- Good control of particle entrainment

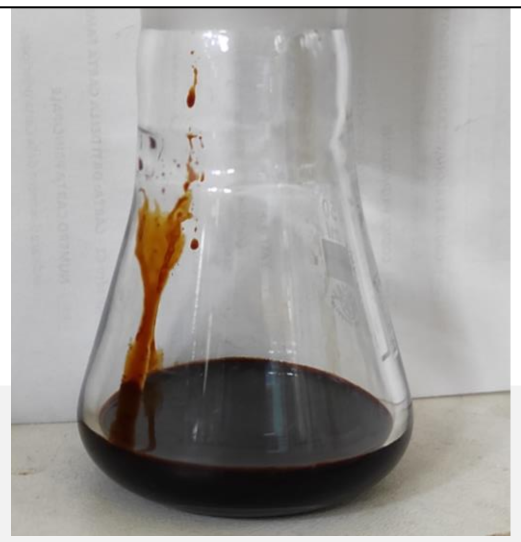
AUGER FUNCTIONING PRINCIPLE



Desing and construction of the pyrolysis plant



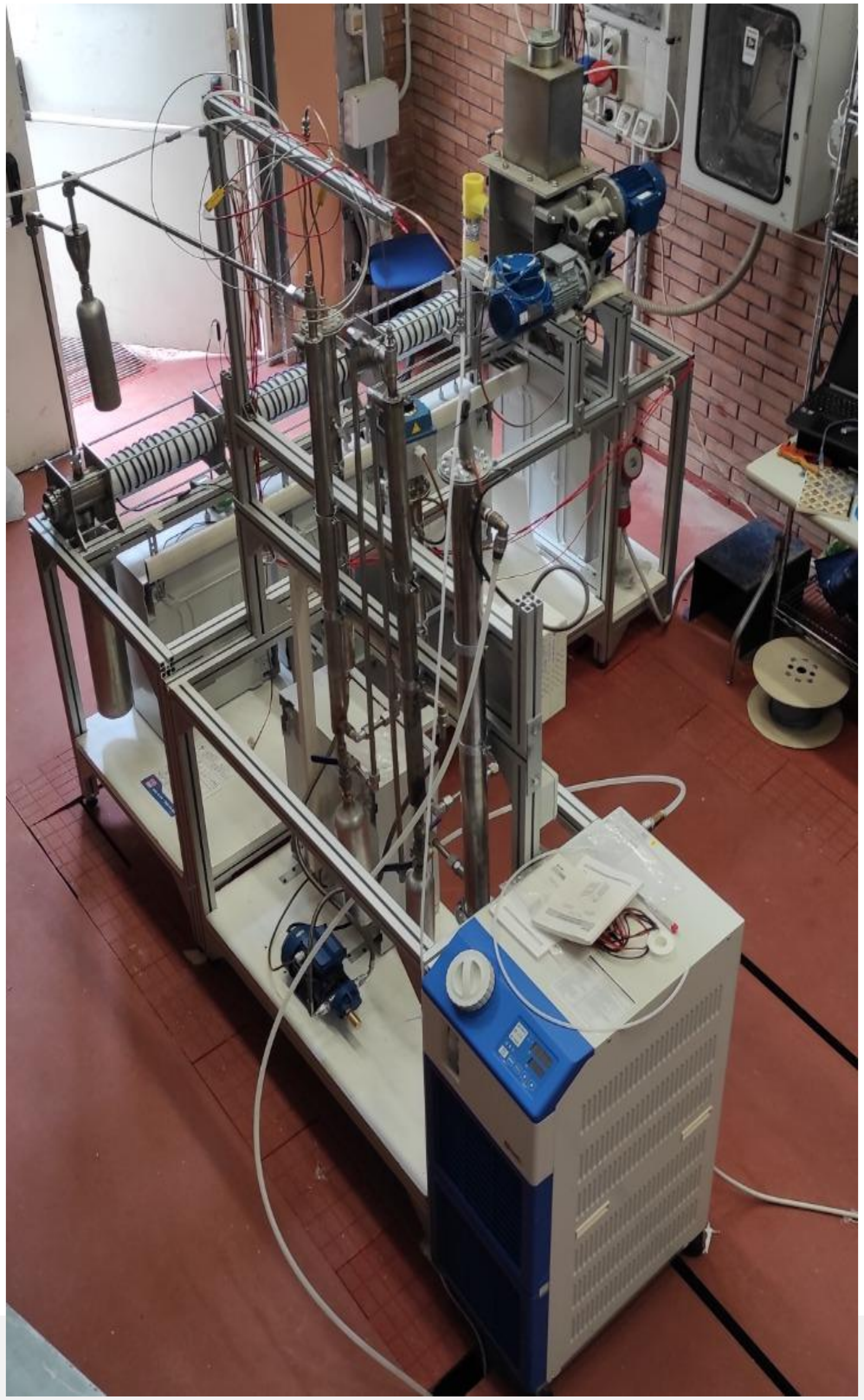
Oily fraction, Condenser I T=90°C	Aqueous fraction, Condenser II T=15/20°C



Desing and construction of the pyrolysis plant

Operating conditions	
Biomass feeding rate	Up to 2 kg/h
Maximum temperature	600 °C
Solid residence time	Up to 18 min

- ✓ 11 biomasses tested
- ✓ Tests at different pyrolysis temperature, carrier gas flow rate, solid residence time



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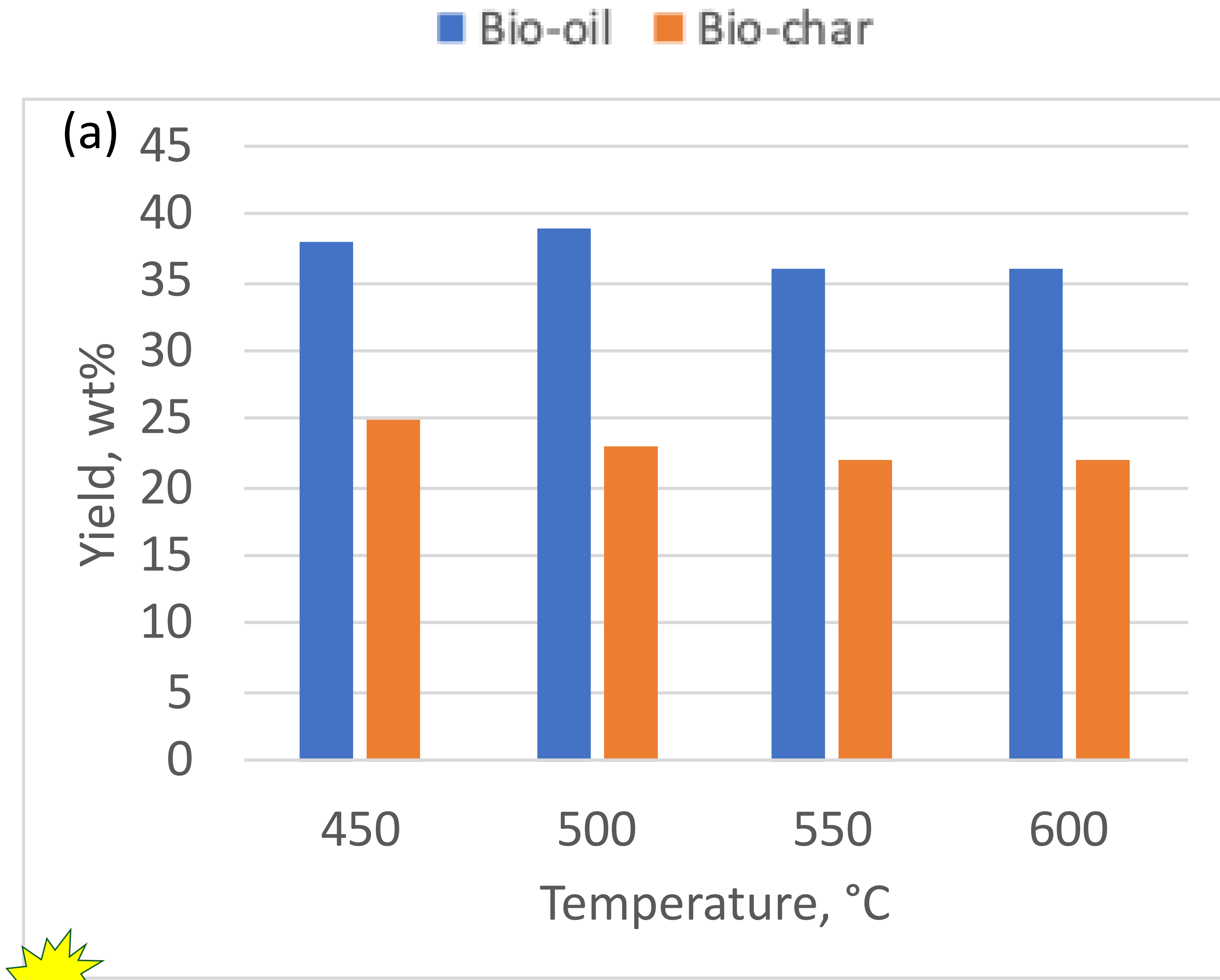
Effect of temperature: Important knowledge gained

Temperature

- to maximize the liquid yield, pyrolysis should be conducted at 500 °C
- To increase liquid quality (reduce water content) temperature should be rised to 600 °C)
- Zn displacement increases greatly from 550 to 600 °C

Test n°	4	5	6	7
Biomass type	Phalaris			
Temperature, °C	450	500	550	600
Water content, wt%	79.2	75.3	72.3	69.6
Solid content, wt%	0.46	0.56	0.52	0.53
Zn Content, ppm	43	43	78	232
Zn displacement in the liquid, wt%	8	8	15	51

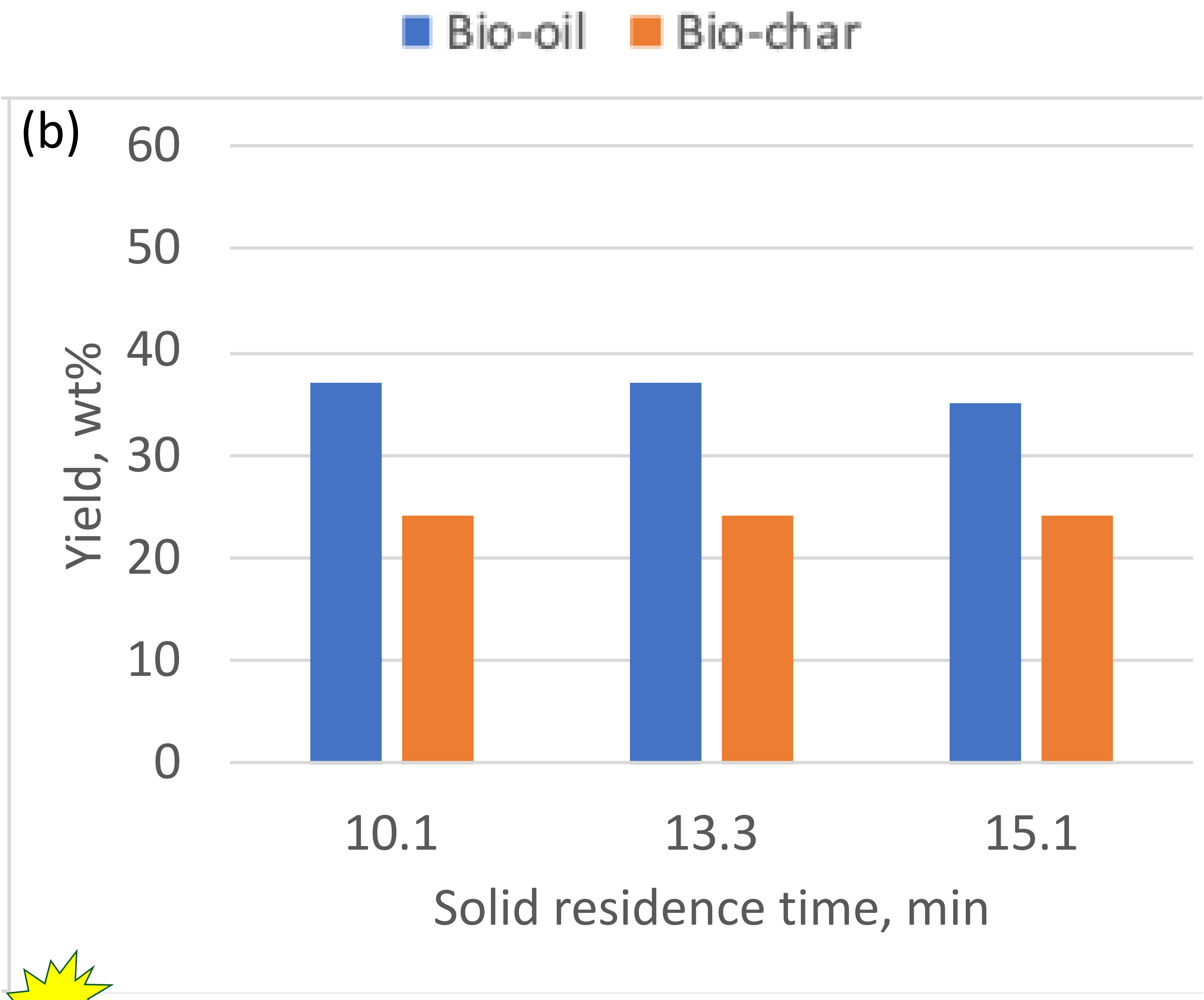


Take away message
The choice of the optimal temperature depends on the initial biomass contamination level

Effect of solid residence time: Important knowledge gained

Solid residence time

Biomass	HH/SRC_UoS/21		
Solid residence time, min	10.1	13.3	15.1
N_2 flow rate, Nl/min		12	
Water content, wt%	63.8	65.1	62.4
C, wt%	19.5	18.7	19.9
H, wt%	9.5	9.8	9.1
N, wt%	n.d.	n.d.	n.d.
O, wt%	71.0	71.5	71.0
Solid content, wt%	0.19	0.13	0.11
Contaminant content, ppm	619	606	598
Contaminant displacement in the liquid, wt%	86	84	78



As solid residence time increases:

- the yield of the liquid remained almost unchanged as well as its water content
- Solid and contaminant content decrease

Take away message

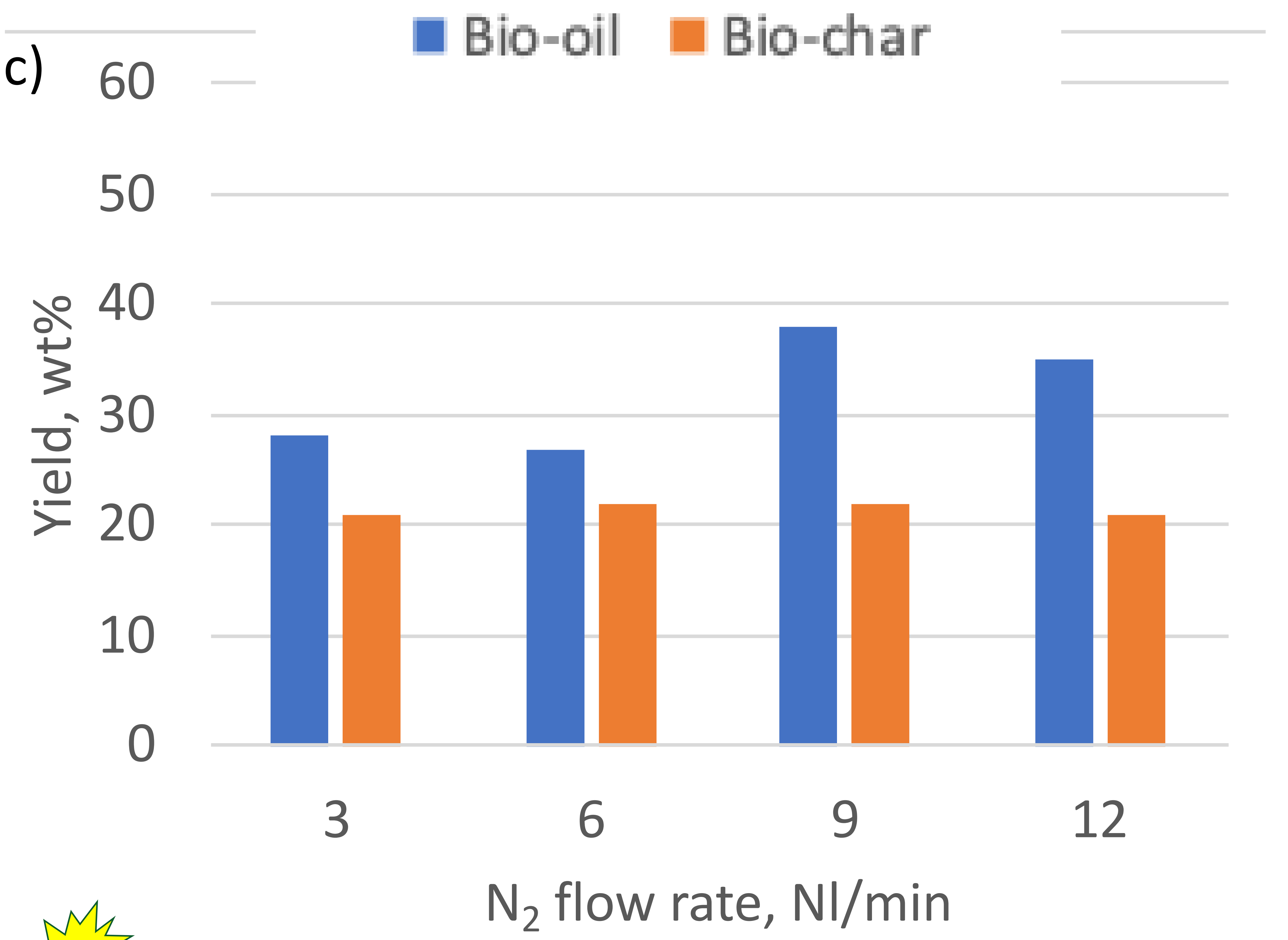
High rotation speed of the screw favors fines formation and negatively affects the liquid yield

Effect of nitrogen flow rate: Important knowledge gained

Vapor residence time

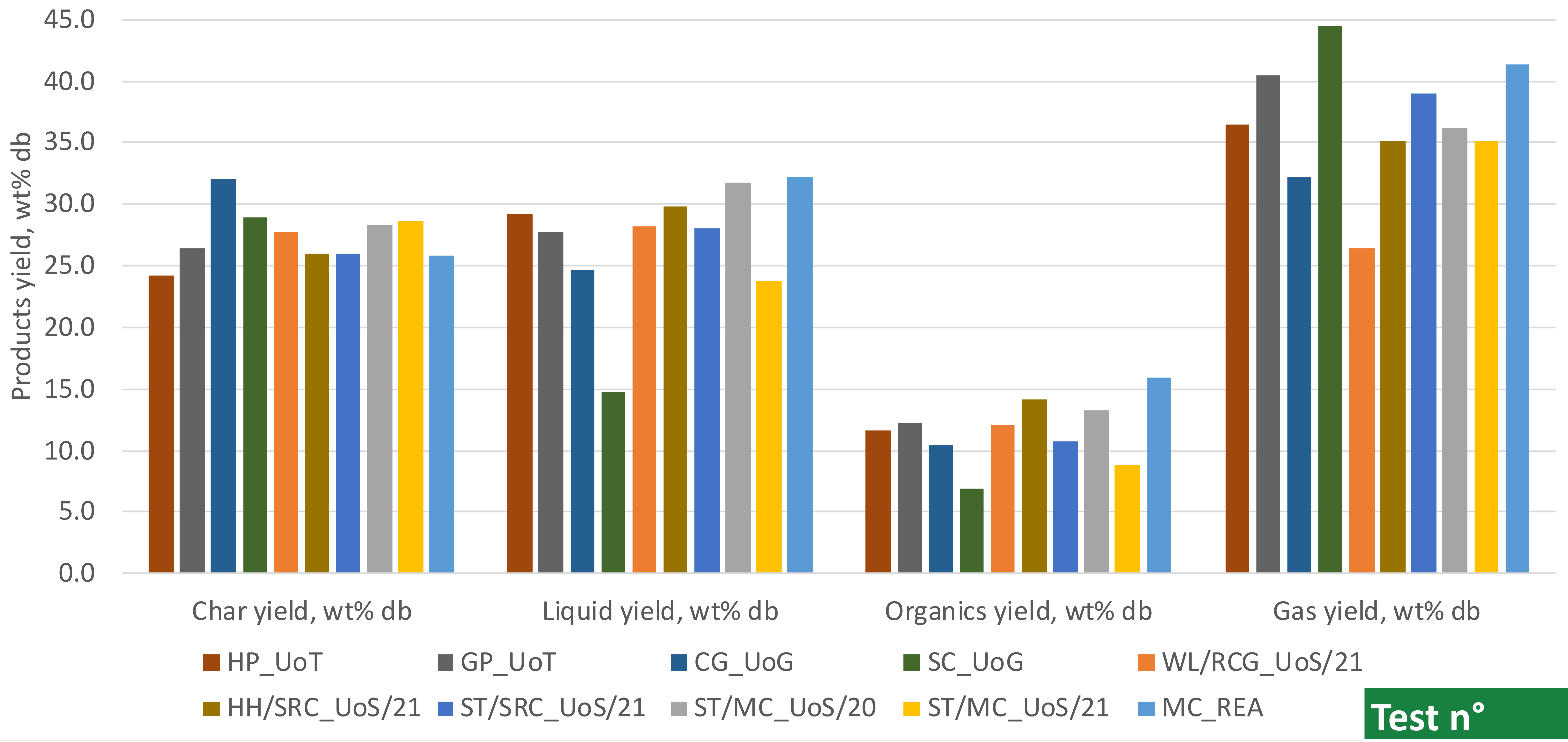
Biomass	P_CNR	
N_2 flow rate, Nl/min	12	9
Solid residence time, min	13.3	
Water content, wt%	43.2	52.7
C, wt%	19.5	18.7
H, wt%	9.5	9.8
N, wt%	n.d.	n.d.
O, wt%	71.0	71.5
Solid content, wt%	0.69	0.31
Contaminant content, ppm	36	36
Contaminant displacement in the liquid, wt%	54	50

- Low N2 flow rate negatively affects heat transfer in the pyrolysis reactor and in the consensation unit
- Liquid yield has a maximum as N2 flow rate increases
- Water content decreases as N2 flow rate increases



Take away message
Liquid contamination is not affected by the carrier gas flow rate

Reactor flexibility with different feedstocks

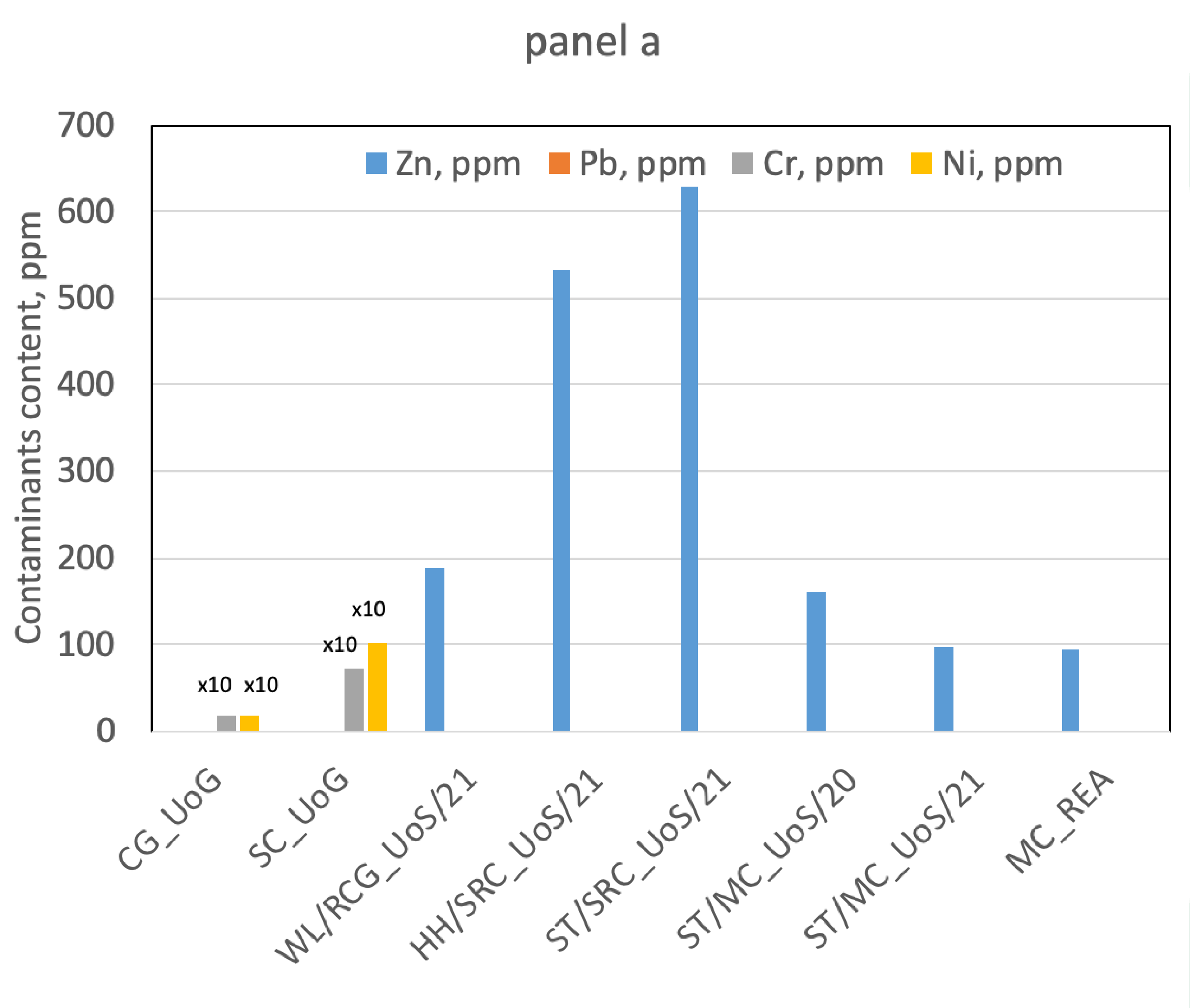


- ❖ Liquid yield has an **average value of 27.0 wt% db** (STD=4.8%).
- ❖ The average value of the organics yields is **11.6wt%** (STD= 2.4%)

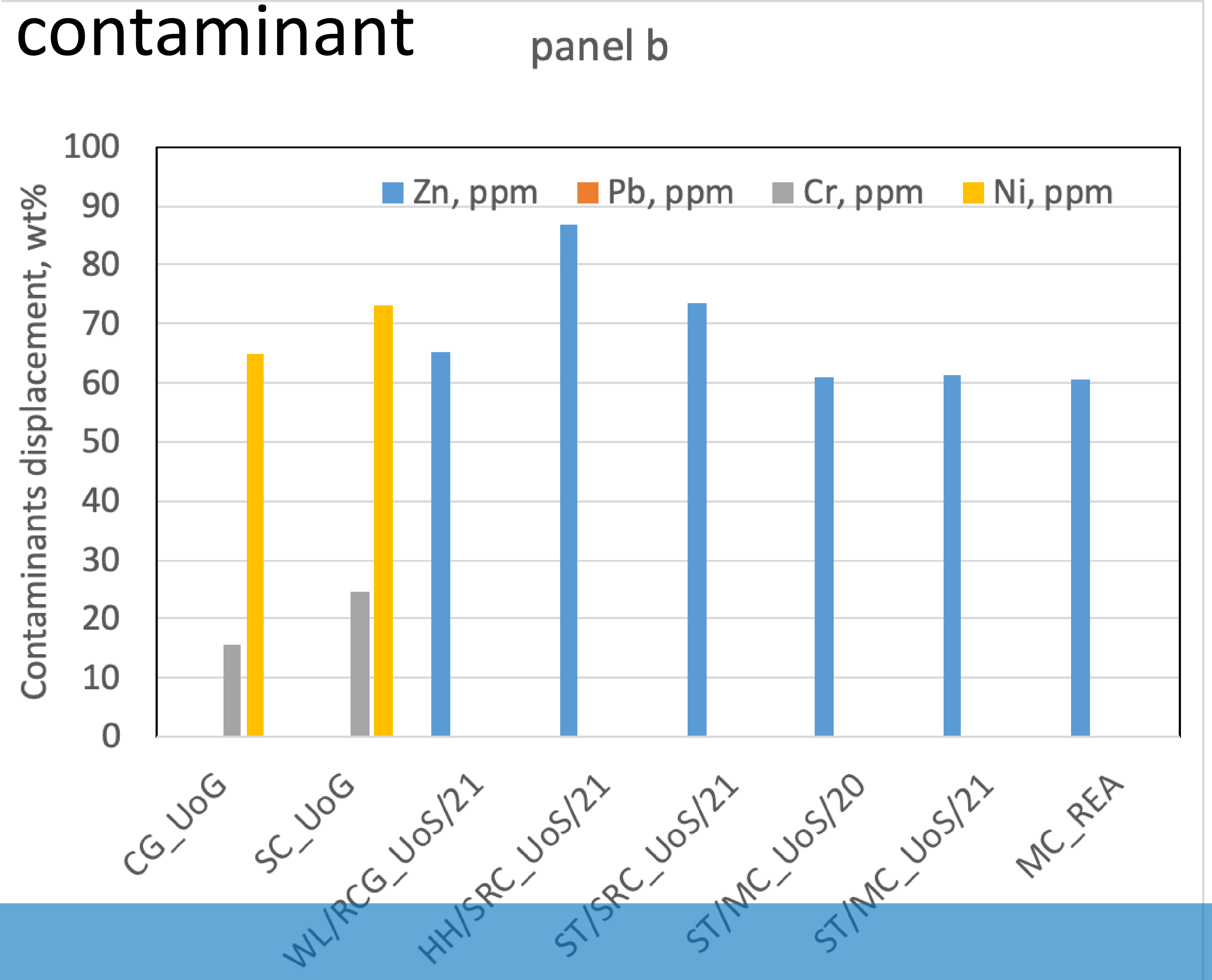
- ❖**The lower the ash content** of the initial **biomass the lower the water content** in the liquid
- ❖The **solid content is very variable**, thus indicating that the formation of fines is dependent on the quality of the pellet, which, in its turn, depends on the biomass composition

Test n°	Mean	ST DEV
Water content, wt%	56.9	4.0
C, wt%	18.7	3.9
H, wt%	8.9	0.8
N, wt%	0.0	n.d.
O, wt%	72.5	3.7
HHV (organic phase), MJ/kg	17.1	4.3
Solid content, wt%	0.13	0.16

Liquid characterization: different feedstocks, heavy metals concentration and displacement



- The displacement of the contaminants slightly depend on the initial content in the biomass and the biomass type, but is strongly dependent on the type of contaminant



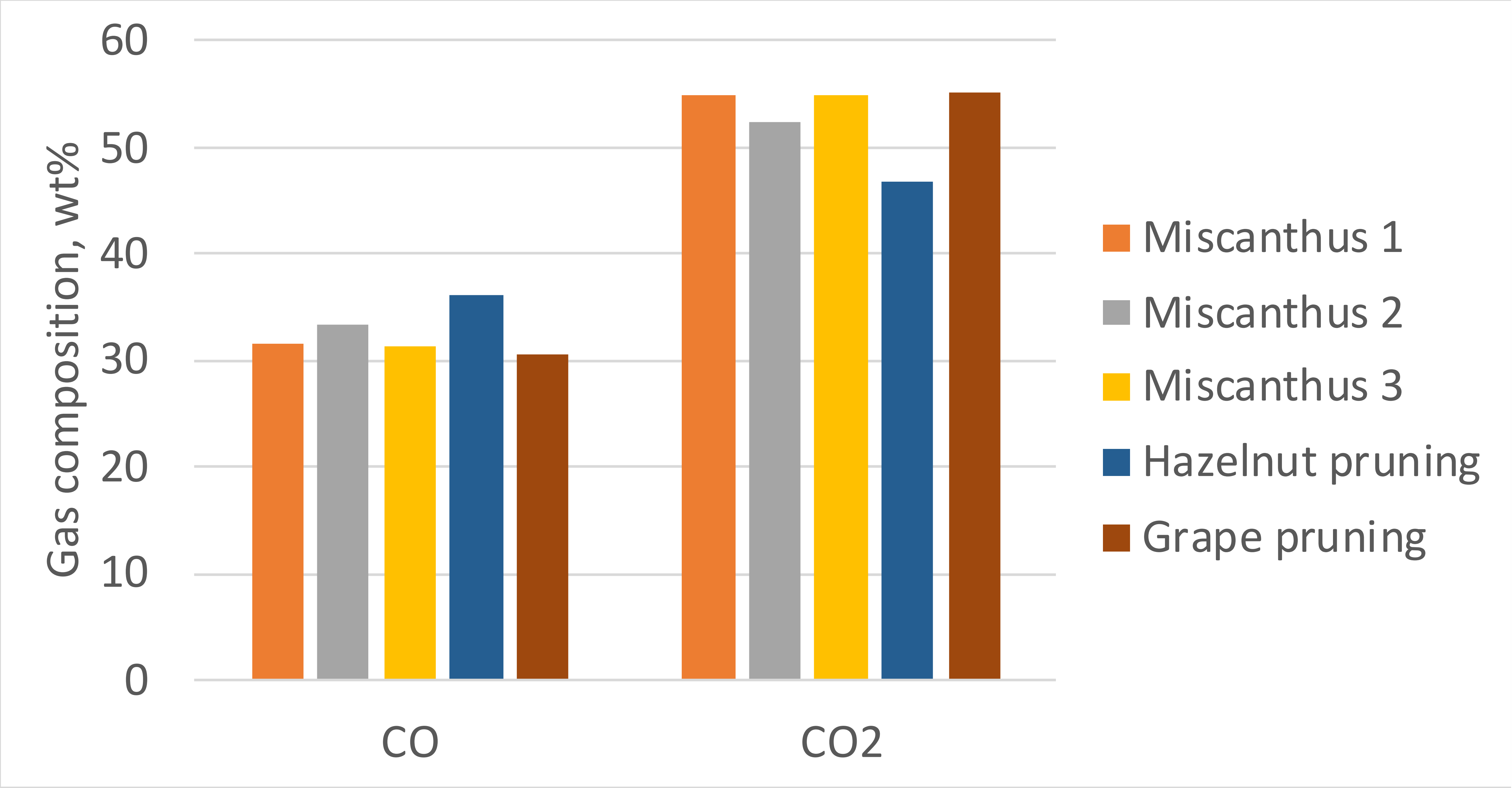
- Cr exhibits a different behavior, characterized by lower displacement in the liquid than Zn and Ni.

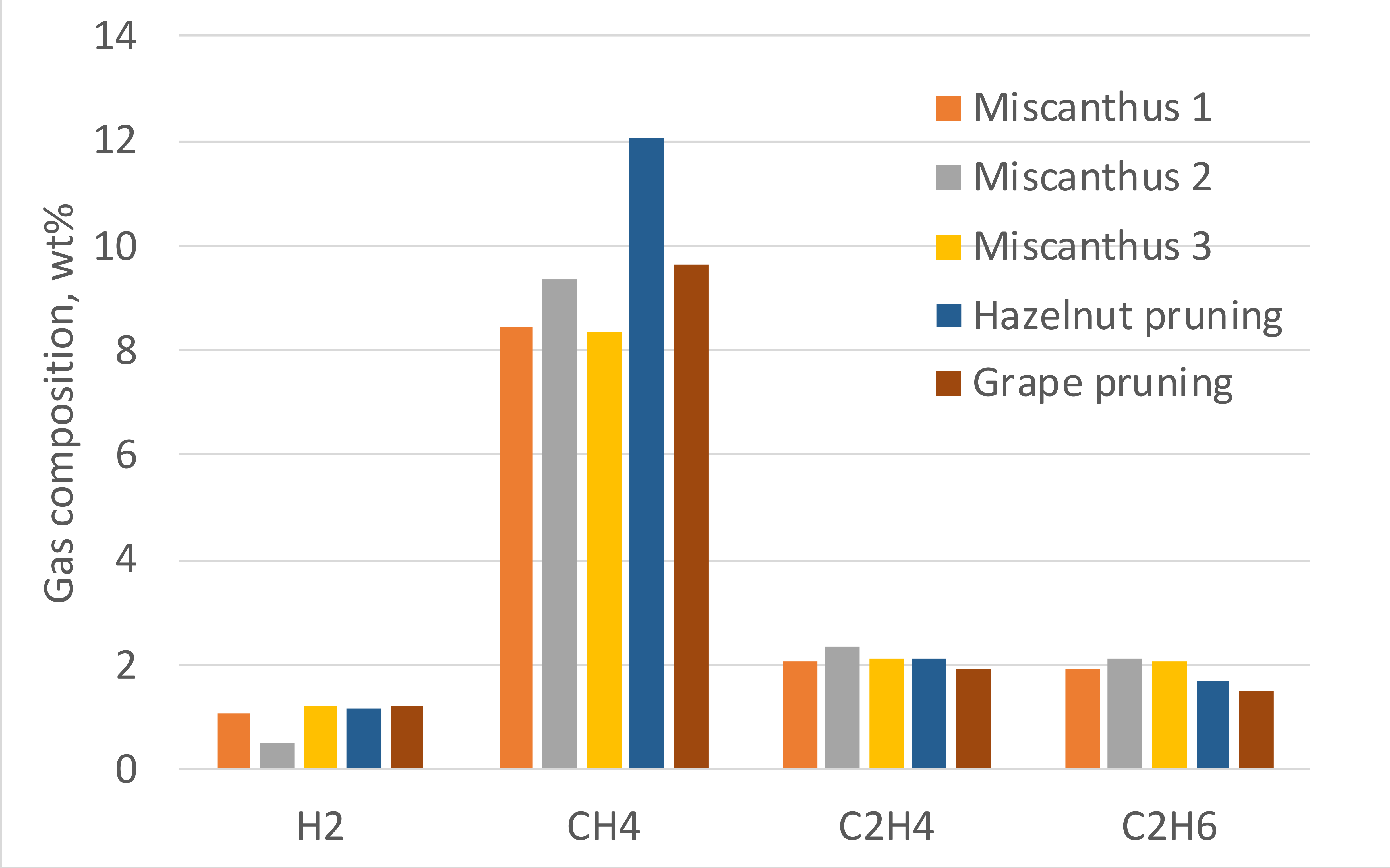
Take away message

To increase liquid quality biomass with lower ash yield should be selected, Pyrolysis temperature can be selected based on the contaminant type and the initial level of the contamination

Gas composition: important knowledge gained

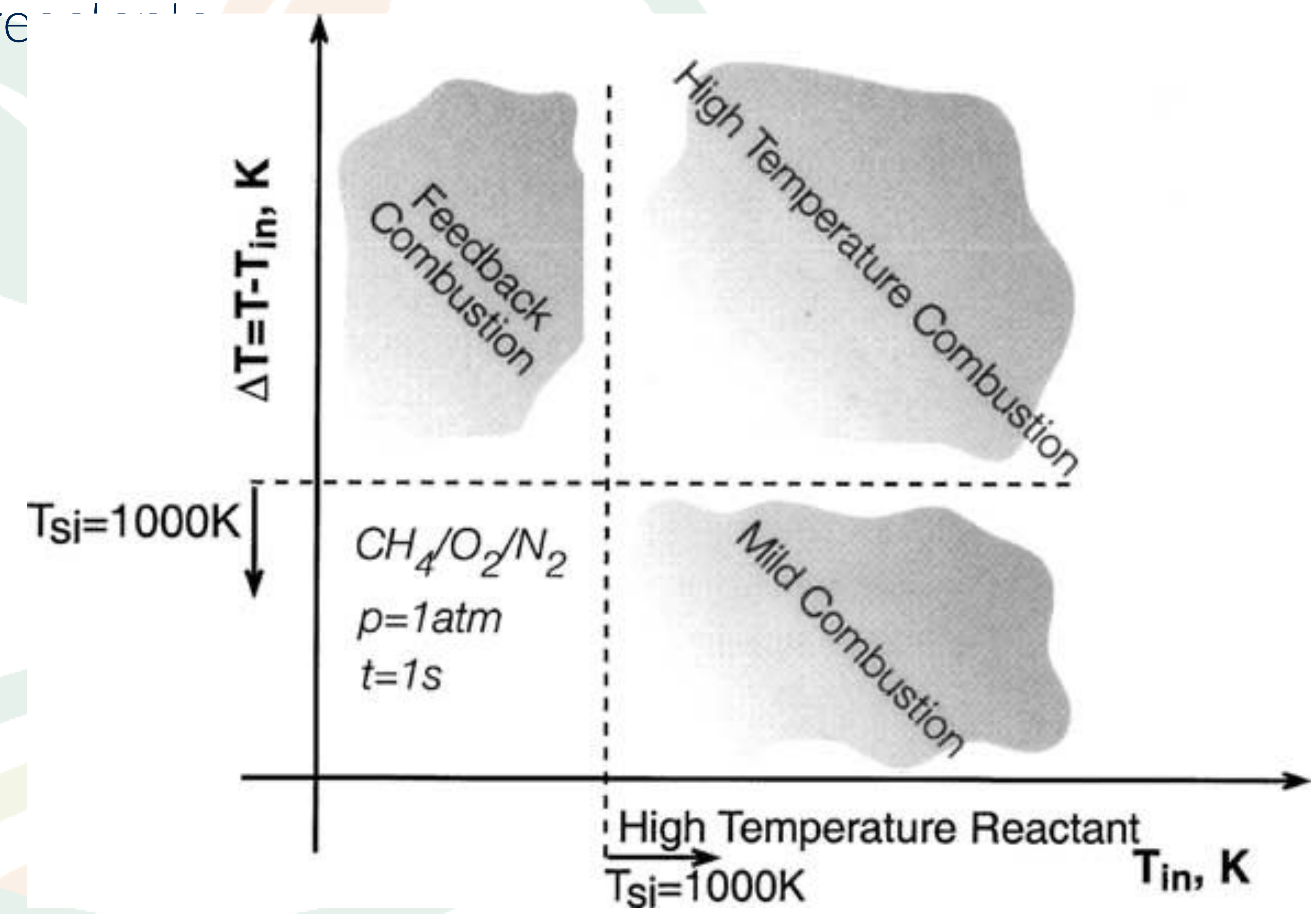
No significant difference in the pyrolysis of different CERESiS biomasses **regarding the gas yield** (31-37 wt%) **composition and HHV** (11 MJ/kg) except for hazelnut pruning (44 wt% and 13 MJ/kg)





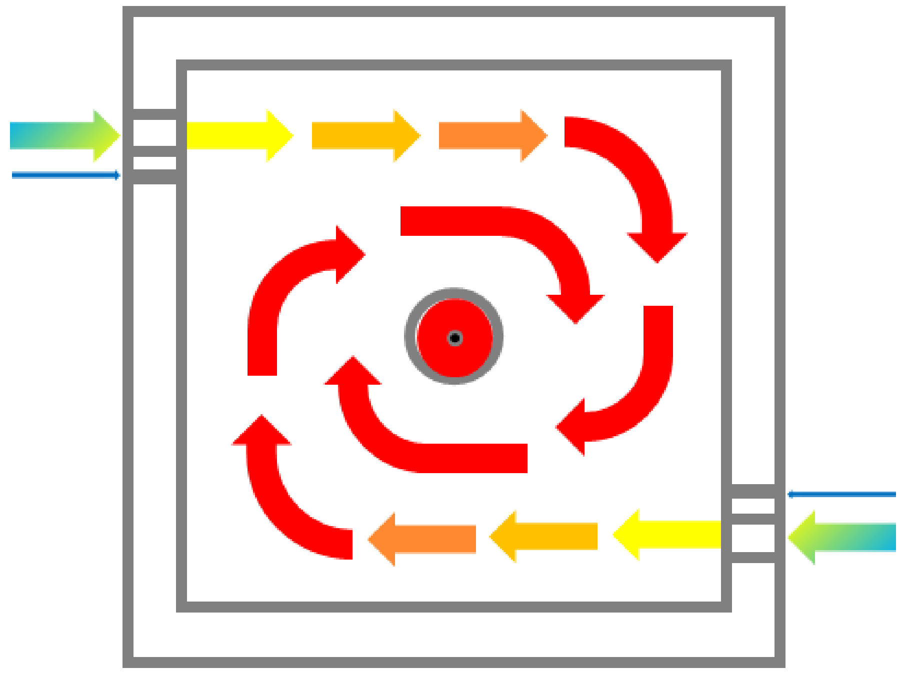
MILD combustion

MILD COMBUSTION: diluted combustion, recirculation of hot exahusted gases towards fresh reactants



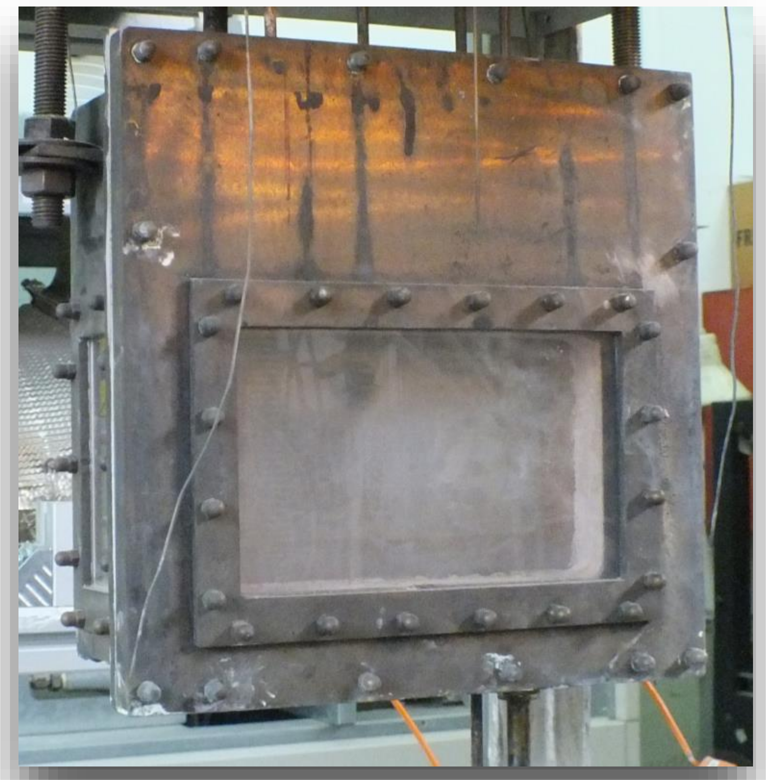
Cavaliere and de Joannon, 2004

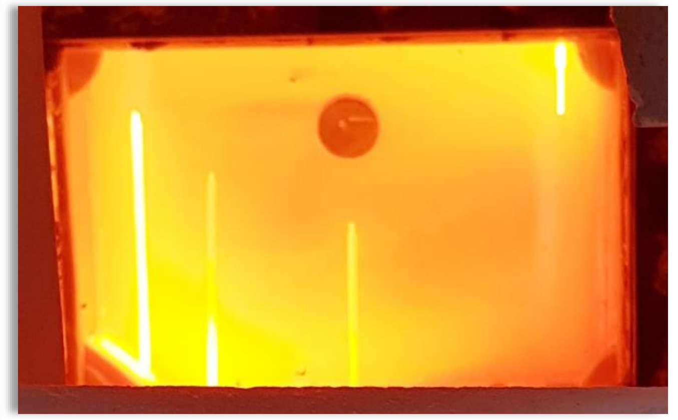
Cyclonic FLow

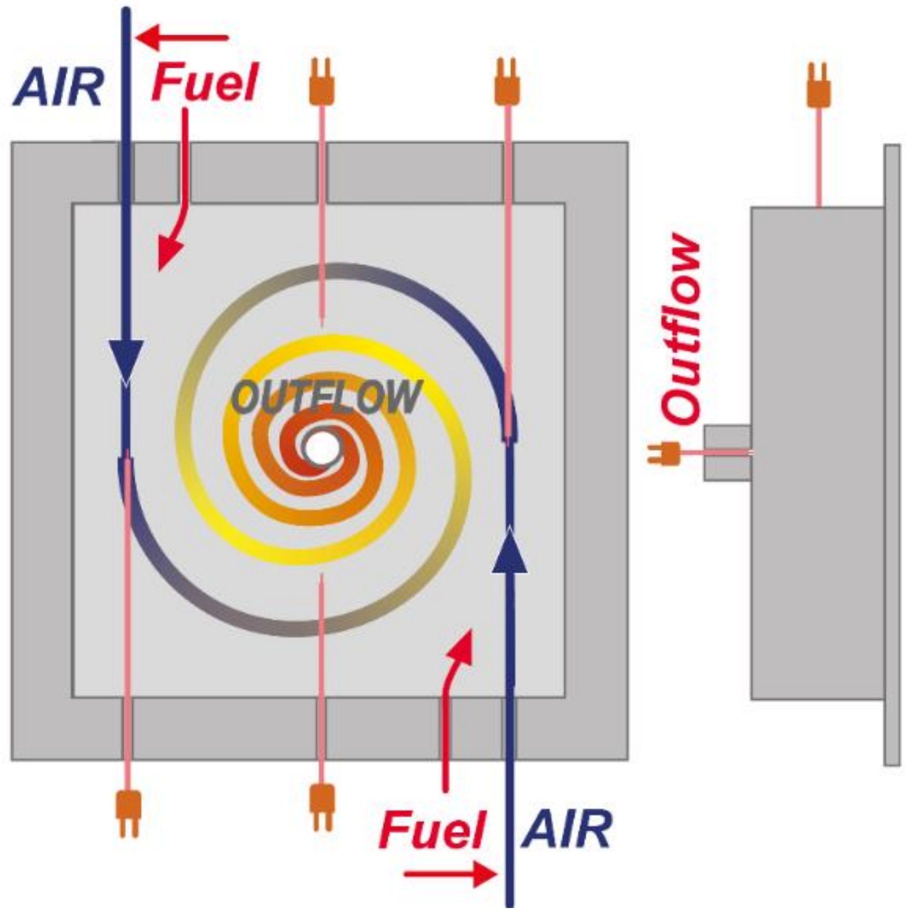


Cyclonic burner for MILD combustion

- ***Height***: *50 mm*
- ***Section***: *200x200 mm²*
- ***Material***: *Alumina/Steel*







PARAMETER	OPERATING RANGE
Thermal power (P_{th})	*Up to 15 kW*
Fuel	*Natural gas - NH_3 – Alcohols – Hydrocarbons – Biogas*
Preheating temperature (T_{in})	*300 ÷1300 K*
Feeding Configuration	*Premixed – Non Premixed*
Equivalence ratio (F)	*Fuel-Lean to Fuel-Rich*
Pressure (P)	*1 atm*

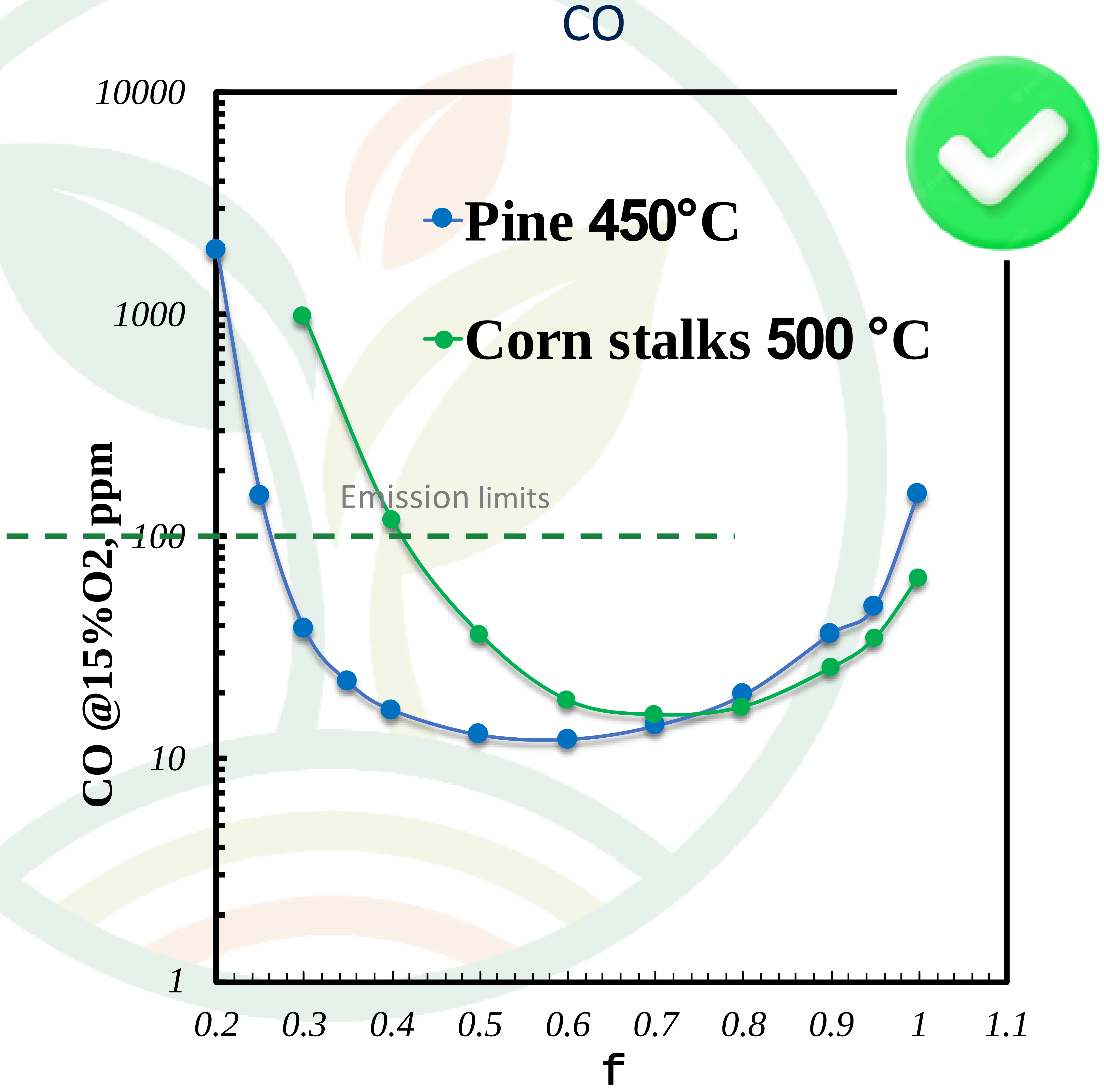
Laboratory-scale combustion tests of pyrolysis gas: stable operation

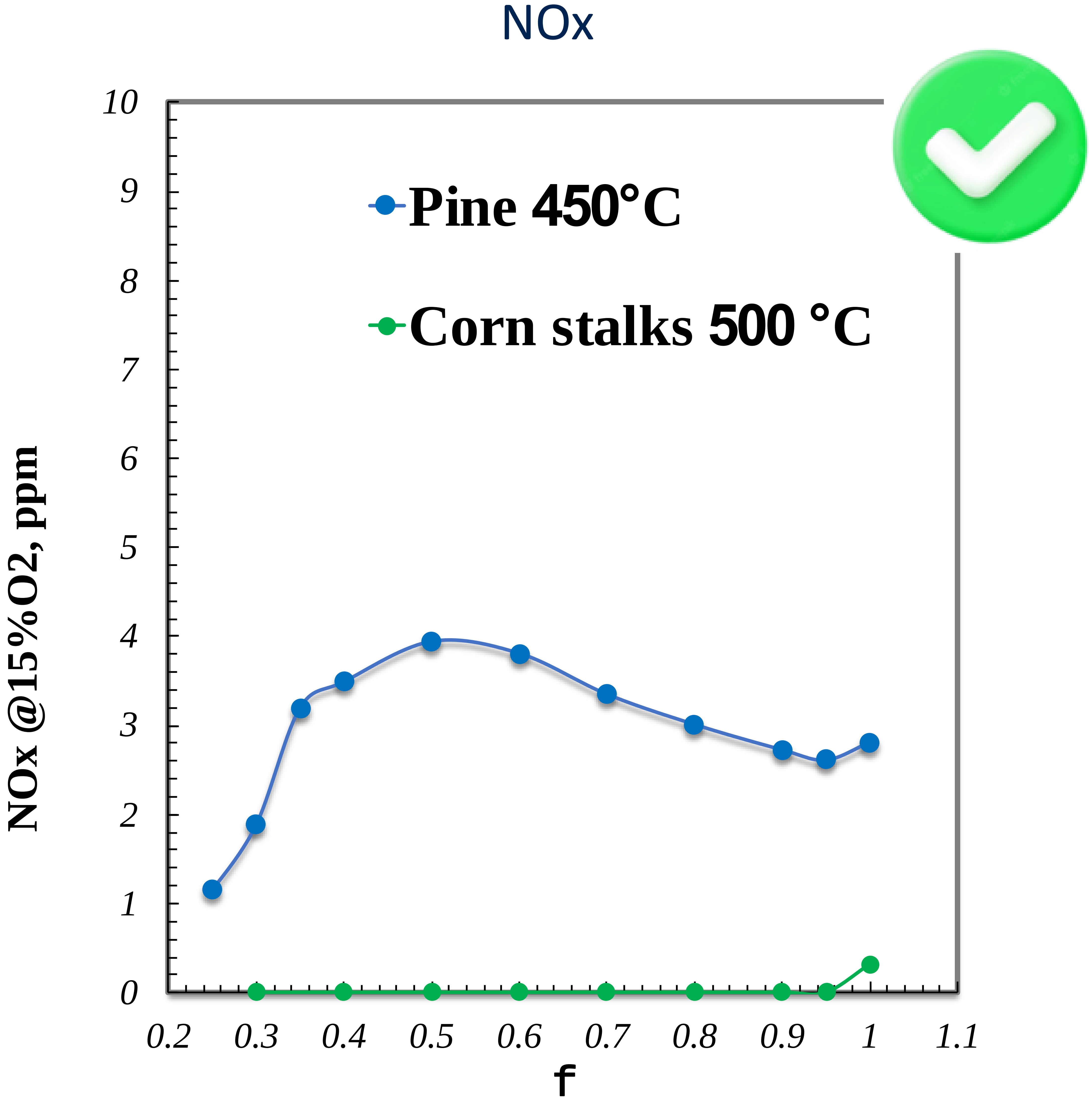
4 surrogate mixtures were selected to take into account the feedstock variability

Species	Rice husks	Corn stalks		Pine
	450	450	500	450
	✔	✘	✔	✔
CO_2	67	79.2	71.4	43
CO	24	15.2	16.1	39
CH_4	6	2.6	8.3	9
C_2H_4	3	3.0	4.1	2
C_2H_6				2
H_2	0	0.0	0.0	3
LHV (MJ/Kg):	3.73	2.56	3.79	7.29

- ✓ For **LHV>7 MJ/Kg** → combustion without pre-heating
- ✓ For **3 <LHV<7 MJ/Kg** → stable combustion with pre-heating (730K)
- ✓ For **LHV < 3 MJ/Kg** → **no stable combustion,** but **H_2 addition, feeding configuration, heat exchange improvement, higher pre-heating levels** represent further chances to stabilize the process

Laboratory-scale combustion tests of pyrolysis gas: emissions





Conclusions

- Pyrolysis using **screw reactor is a viable technology** to treat HM contaminated biomass
  - The most critical parameters affecting the **bio-oil yield and quality are temperature and carrier gas flow rate**, whereas temperature mainly controls **bio-oil contamination**
  - The choice of the optimal temperature should be done taking into account the type of contamination and the initial contaminants content in the biomass

- **Stable and sustainable combustion of pyrolysis gas** was successfully obtained in a cyclonic burner operating under **MILD combustion** regime

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