Bio-Flex CLC

Flexible chemical looping combustion for combined heat and power production from biogenic residues with negative emission

Assessment of the Chemical Looping Combustion of biomass from the operation of a pilot unit at the 20 kWth scale

L.F. de Diego, M.T. Izquierdo, A. Filsouf, F.J. García-Labiano, A. Abad

M.T. Izquierdo: mizq@icb.csic.es

GHGT-18

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Outline

- Decarbonization in the EU
- The Bio-FlexCLC project
- Chemical Looping Combustion (CLC) concept
- Experimental campaigns and results
- Ongoing work

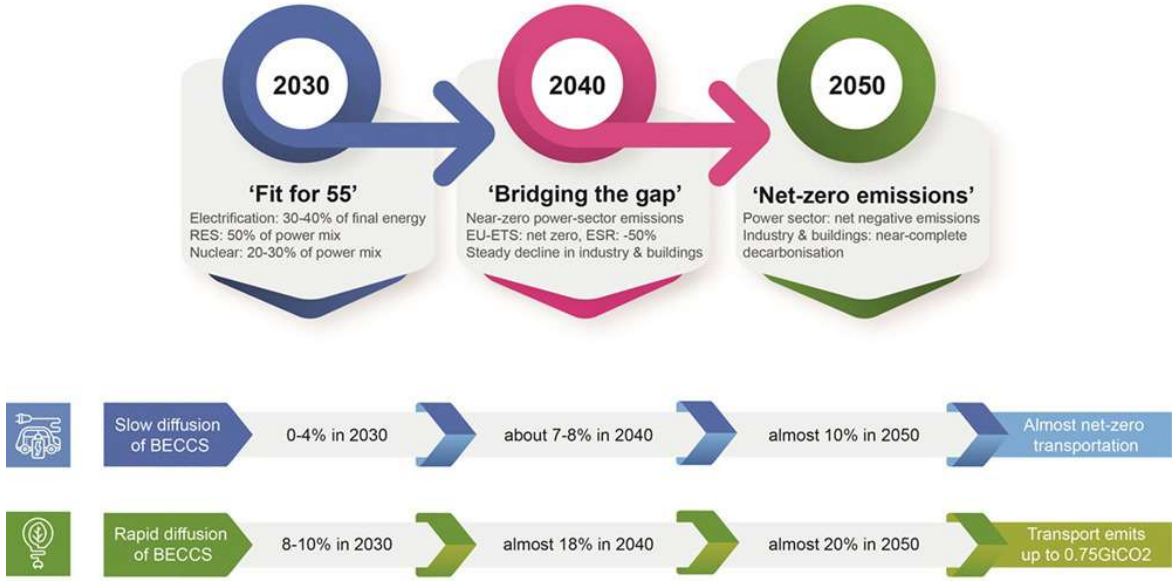
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CSIC Consejo Superior de Investigaciones Científicas
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Decarbonization in the EU

- EU has committed to full decarbonization in less than 30 years and Carbon Dioxide Removal (CDR) including Bio-Energy with Carbon Capture and Storage (BECCS) will be instrumental if this is to be achieved.
- However, the high cost and energy penalties of CCS are considered one of the most important barriers to the implementation of CCS and BECCS.
- Moreover, in light of no policy instruments and economic incentives currently in place for BECCS while at the same time needing rapid and substantial BECCS, it poses a dilemma for end users.

➢**Need to minimize the risks of investment in BECCS**



Source: *A multi-model analysis of the EU's path to net zero. Boitier et al. Joule 2023, 7, 2760–2782*

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https://www.bioflexclcproject.eu/

Bio-FlexCLC
Flexible chemical looping combustion for combined heat and power production from biogenic residues with negative emissions

The **goal** of Bio-FlexCLC project is to establish an efficient and scalable process to convert low-value biogenic residues and organic waste to heat and power with **negative or zero emission** through Chemical Looping Combustion (CLC)-Circulating Fuidized Bed (CFB) coupled with gas cleaning and CO_2 liquefaction

Participants: 10 consortium partners from 7 EU countries

Partner	Role
RISE	Project coordination, process design and technoeconomic assessment, LCA and sLCA, developing gas cleaning and liquefaction processes
Repotec	Designing the process and operating strategies
GMAB	Designing gas treatment technologies
CTH	Improving process performance of flexible Bio-FlexCLC
CSIC	Chemical looping and fluidized bed combustion
CERTH	CFD modelling of post-oxidation chamber and fuel reactors with packings
TUDa	Demonstration of Bio-FlexCLC at MW scale; process evaluation and optimization of flexible Bio-FlexCLC
1Cube	Exploitation, Dissemination and Communication
FORTUM	Providing feedback and data for process and environmental analysis. Utility producer in Poland. Potential end user of the process.
VEAB	Providing feedback and data for process and environmental analysis. Utility producer in Sweden. Potential end user of the process.

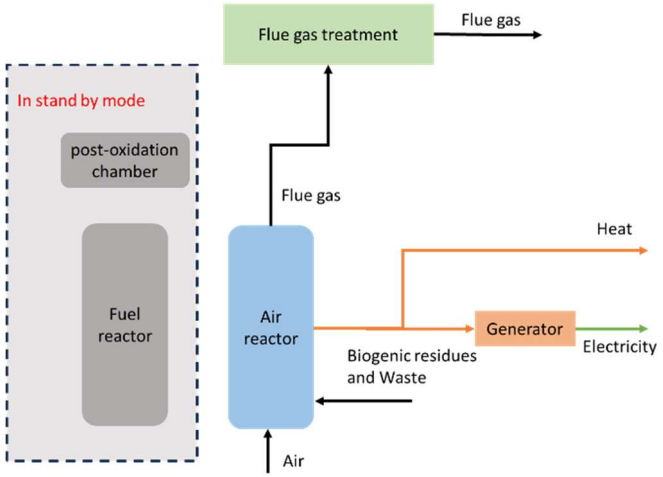


Concept

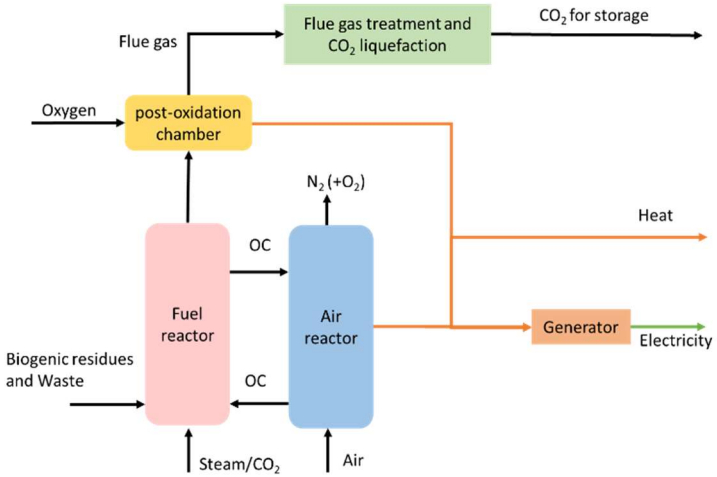
based on dual CFB reactors, which can operate in Chemical Looping Combustion mode while both reactors are in use or switch to conventional CFB operation when only one reactor is in use.

Operating in CLC mode enables Combined Heat and power (CHP) production with negative emissions at low-cost while the concept is flexible to switch to CFB boiler mode to produce CHP with net-zero emissions

Operating in CFB mode



Operating in CLC mode



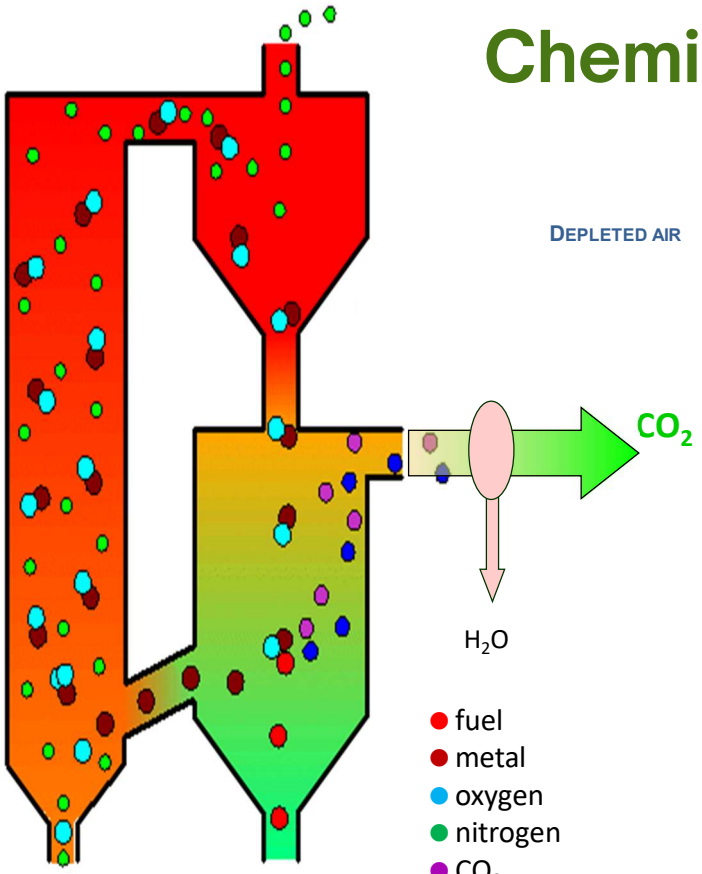
J. Guo et.al. Forests 2024, 15(8), 1372

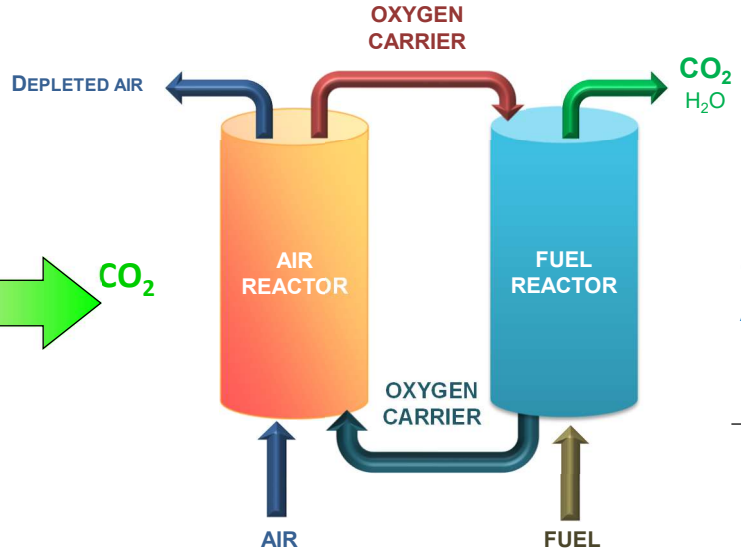


Biogenic waste as feedstock

- **low cost and energy for CO_2 capture** (no gas separation needed)
- 100% CO_2 capture possible while having **low emissions** of NOx, SOx and other harmful components
- **low corrosion** with improved steam data for improved electrical efficiency
- **flexible system** with respect to the heat/power ratio
- **flexibility to operate** the system as a normal circulating fluidized bed without CO_2 capture if conditions are not amiable for this.

Chemical Looping Combustion





FUEL REACTOR:

OC+ Fuel ⟶ Reduced OC +CO_2 + H_2O ΔH_r

AIR REACTOR:

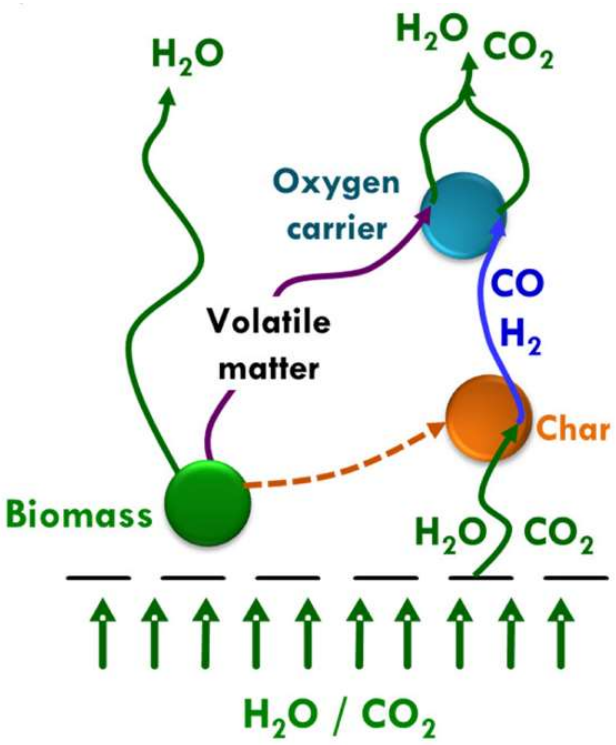
Reduced OC + O_2 ⟶ OC ΔH_o

FUEL + O_2 ⟶ CO_2 + 2 H_2O $\Delta H_c=\Delta H_r+\Delta H_o$

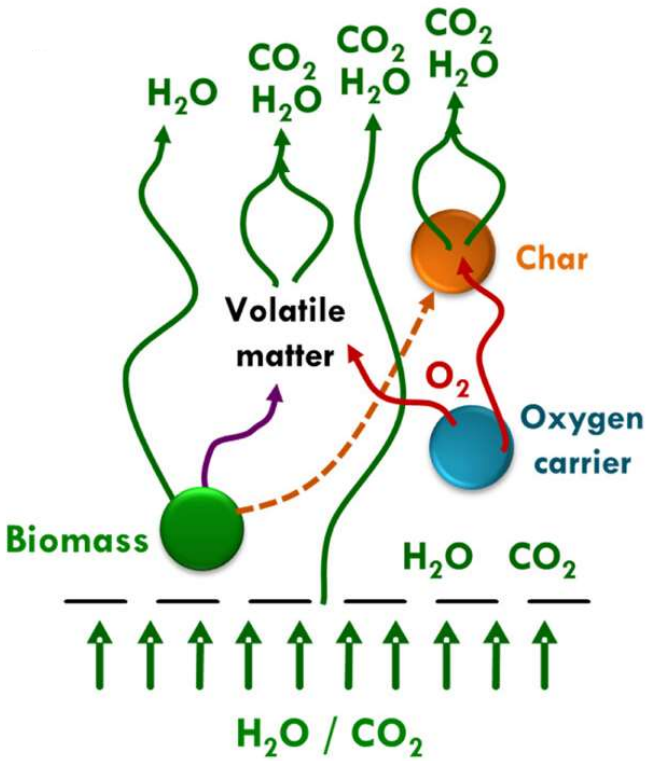
-High selectivity towards CO_2 y H_2O
-Enough oxygen trasnport capacity
-Chemical and mechanical stability along cycles
-Adequate particle size for fluidization
-Environmental friendly
-Low cost

Chemical Looping Combustion

in situ gasification CLC (iG-CLC)



chemical looping with oxygen uncoupling (CLOU)



Experimental campaigns and results

Organic wastes selection
Oxygen carrier
Chemical Looping Combustion unit
Experiments in CFB mode
Experiments in CLC mode

Selected organic wastes






ANALYSIS (wt.%)	Pine wood pellets	Olive stones	Spruce chips	Refused-Derived Fuel
Moisture	7.5	7.3	8.0	2.8
Ash	0.2	0.3	2.5	11.8
Volatiles	77.1	74.9	72.1	76.9
Fixed carbon	15.1	17.4	17.5	8.5
C	47.2	47.8	46.7	55.0
H	5.6	5.3	5.4	6.6
N	0.1	0.2	0.4	0.9
S	<0.1	<0.1	<0.1	0.3
O(by diff.)	39.4	39.1	37.0	22.6
Cl (g/kg)	0	0	0.2	9.0
LHV (kJ/kg)	17042	17352	16808	23211

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Cl (g/kg)	0	0	0.2	9.0
LHV (kJ/kg)	17042	17352	16808	23211

Oxygen carrier

Ilmenite (natural ore)

100-300 µm particle size

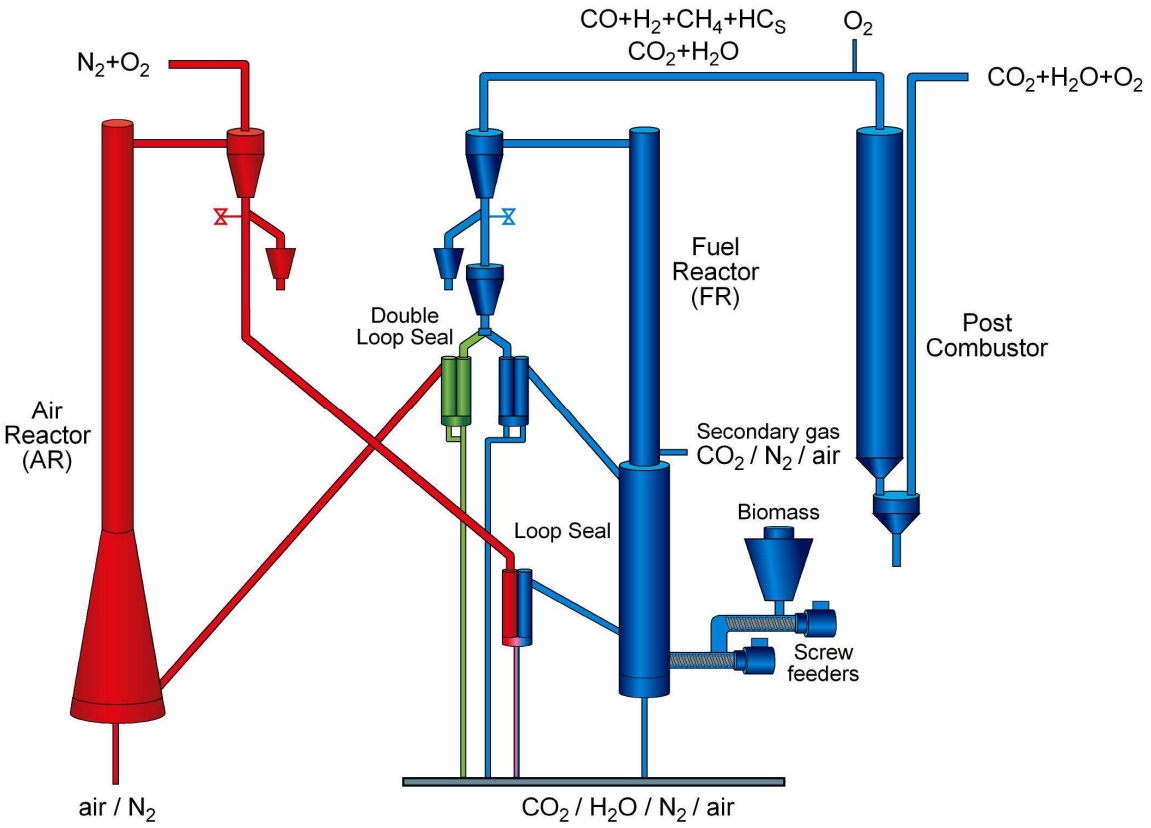


Calcination (950º C 24 h)

Oxygen transport capacity (R_{oc})
4 %

$Fe_2TiO_5/FeTiO_3$

CLC unit for solid fuels (20 kW_{th})

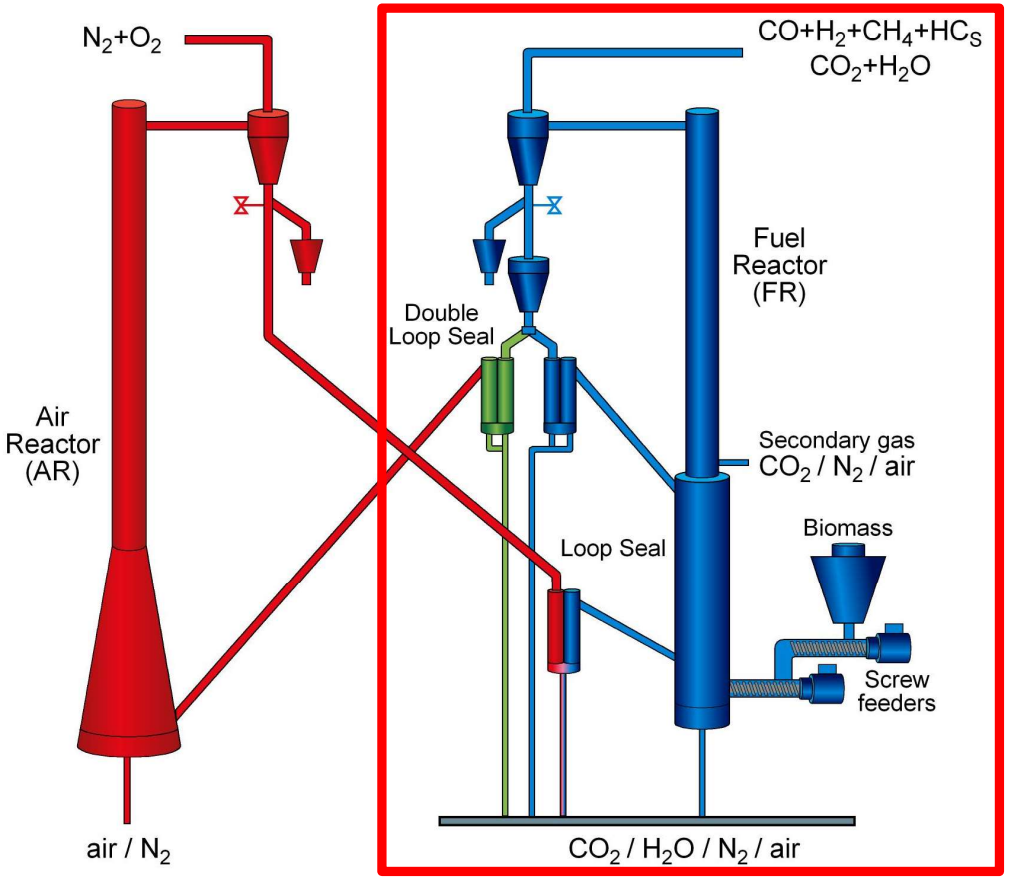




		FR	AR	POC
Height	(m)	4.00	4.80	2.00
Bottom D	(m)	0.10	0.30	0.20
Upper D	(m)	0.08	0.08	0.20

- Built in 2013 with a nominal capacity of 50 kWth for CLOU and 20 kWth for iG-CLC. **Now adapted for Bio-FlexCLC project**
- Double loop seal allowing the independent variation of the solids inventory, solids circulation rate and fluid-dynamic conditions
- On-line gas analyzers and tar collection system.
- Post oxidation chamber (PoC): to fully burn unconverted products

1st experimental campaign CFB Combustion

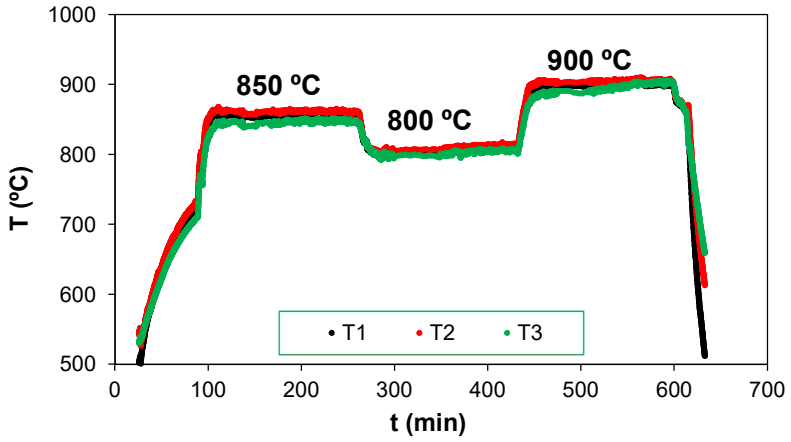


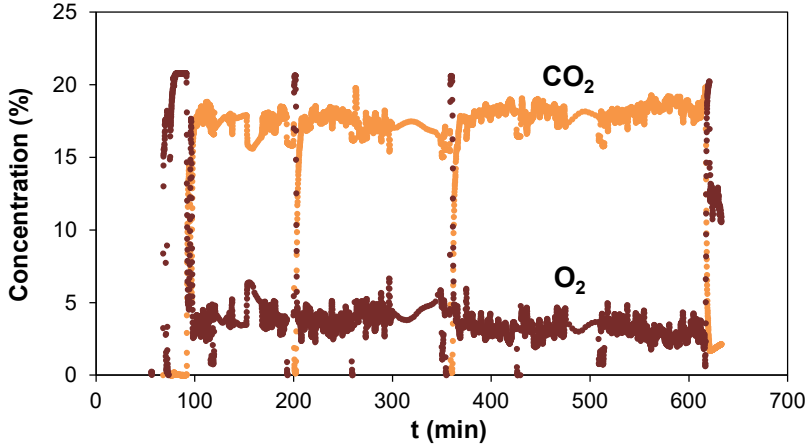
- Bed material: SAND (changed by switching the fuel)
- dp = 100 – 500 μm
- Reference conditions:
  - Temperature: 850 °C
  - Excess air: 20 %
  - Superficial gas velocity: 2.5 m/s (bottom), 5.0 m/s (top)
  - Primary air/total air = 78 %
  - Solids circulation rate: ~20 kg/m^2 s

Experimental variables:

- Temperature: 800 – 900 °C
- Excess air: 10 – 30 %
- Superficial gas velocity: variation in the secondary/primary air ratio

1st experimental campaign CFB Combustion





Thermal power ≈ 20 kW

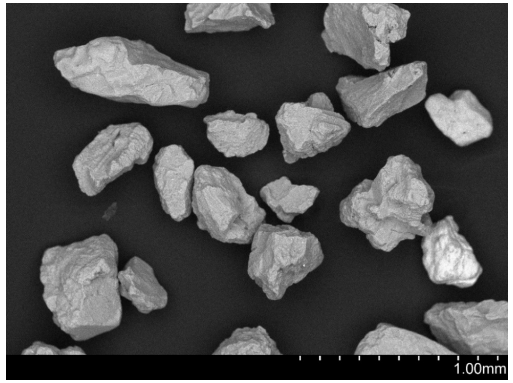
Combustion eficiency > 98%

Comparative emissions under reference operating conditions (850 ºC, 20% air excess)

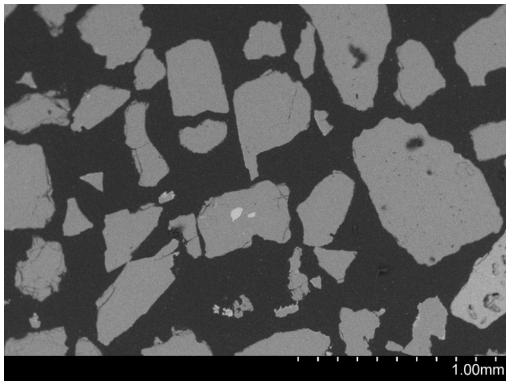
	CO_2	O_2	CO	SO_2	NO	NH_3	Tars
	%	%	vppm	vppm	vppm	mg/kg bio	mg/kg bio
Pine pellets	16.2	3.9	545	0	81	0	0.23
Olive stone	17.5	3.3	6910	0	140	0	0.63
RDF	15.1	3.7	6980	26	239	35.4	1.10
Spruce chips	16.4	3.8	677	0	315	0	0.55

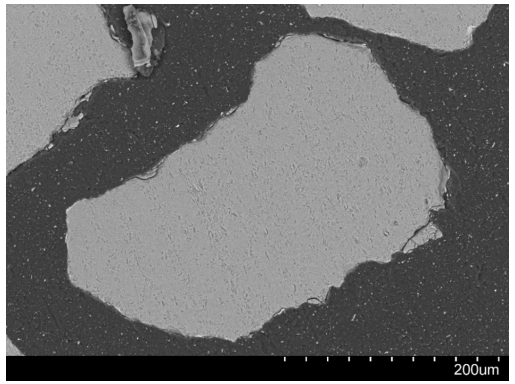
1st experimental campaign CFB Combustion
PINE WOOD PELLETS (fuel)

Entire particle

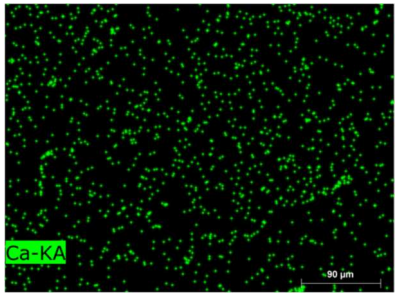


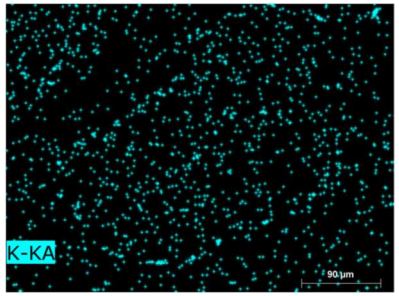
Cross-section

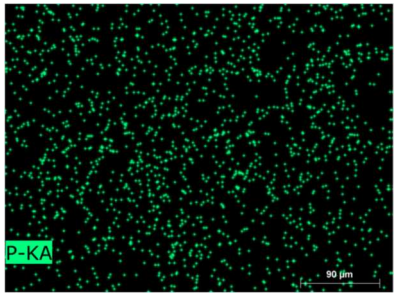




No ash-sand interaction
No agglomeration



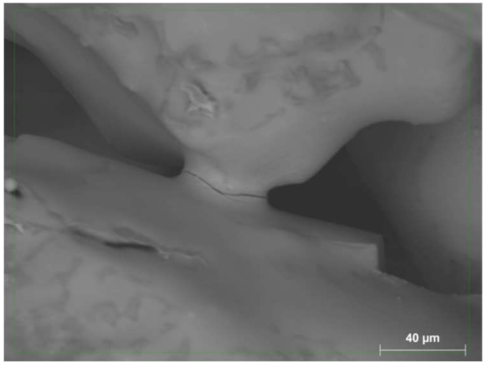


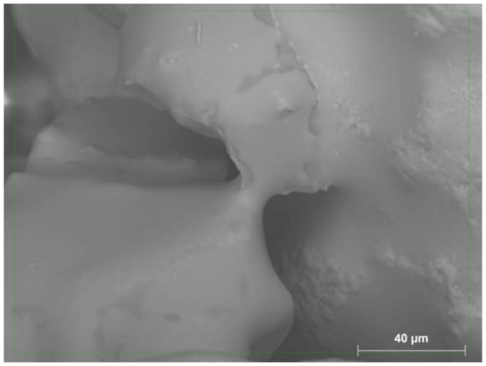


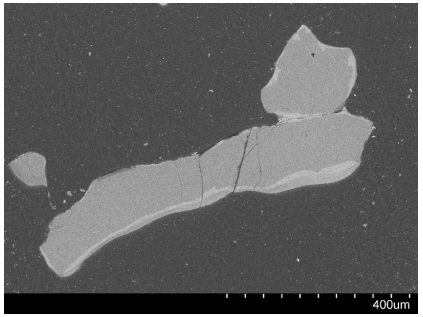
1st experimental campaign CFB Combustion
OLIVE STONE (fuel)



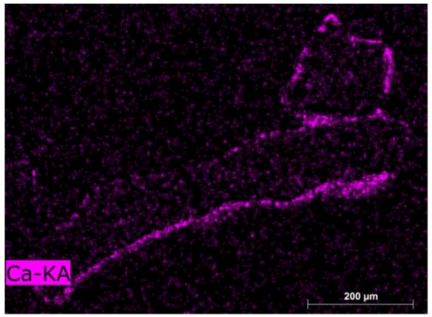
Ash-sand interaction
Agglomeration

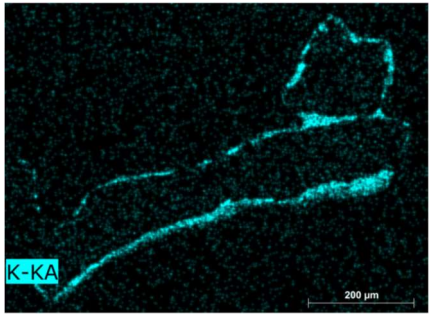






Accumulation: Ca, K



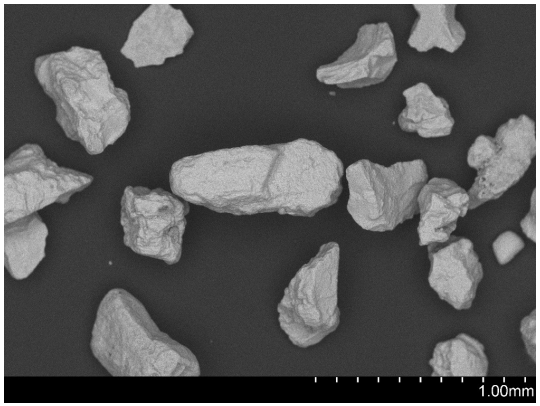


1st experimental campaign CFB Combustion
RDF (fuel)

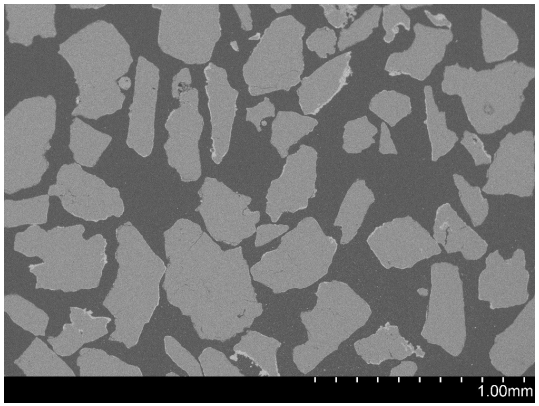
Temperature (˚C)	Excess Air (%)	Primary/total air ratio (%)	CO_2 (%)	O_2 (%)	CO vppm	SO_2 vppm	NO vppm	NO_2 vppm	N_2O vppm	NH_3 mg/kg bio	Tars g/kg bio (g/m^3)
850	**20**	78	15.1	3.7	6980	26	239	13	< 10	35.4	1.10 (0.156)
800	20	78	15.0	3.7	8610	33	292	18	< 10	-	0.62 (0.090)
900	20	78	15.6	3.0	5890	14	202	12	< 10	-	-
850	**30**	78	13.7	5.0	5250	23	280	14	< 10	-	-
850	**10**	78	15.8	2.6	11090	29	260	11	< 10	-	-
850	20	**95**	15.3	3.3	7080	31	272	13	< 10	-	-

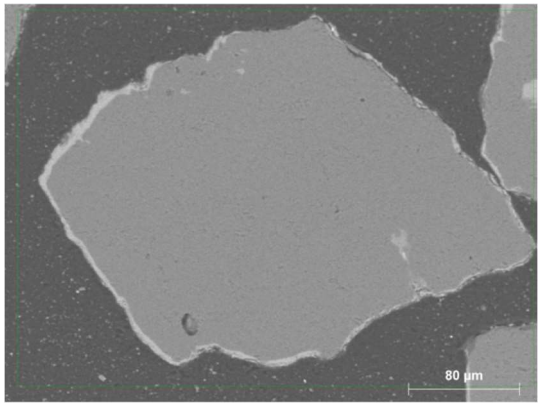
1st experimental campaign CFB Combustion
RDF (fuel)

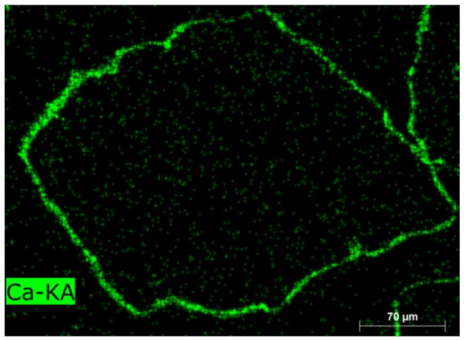
Entire particle

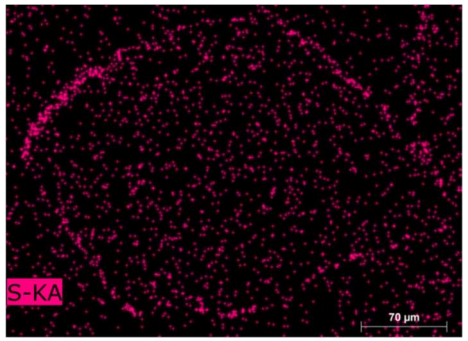


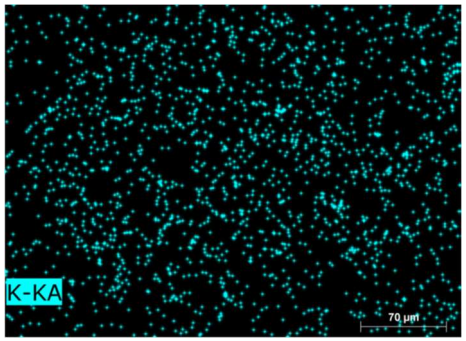
Cross-section





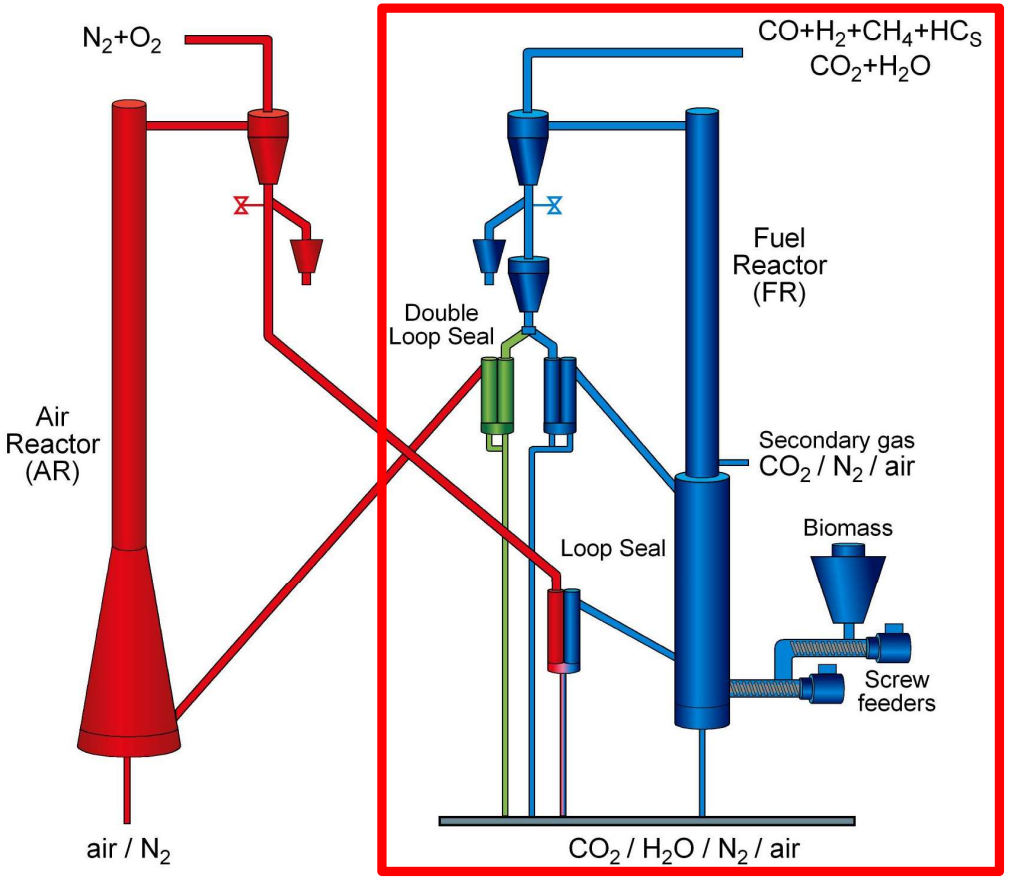






Accumulation: Ca, S

2nd experimental campaign CFB Combustion



- Bed material: ILMENITE
- dp = 100 – 300 μm
- Reference conditions:
  - Temperature: 850 °C
  - Excess air: 20 %
  - Superficial gas velocity: 2.5 m/s (bottom), 5.0 m/s (top)

Experimental variables to be analyzed:

- Temperature: 800 – 900 °C
- Excess air: 10 – 30 %
- Superficial gas velocity: variation in the secondary/primary air ratio

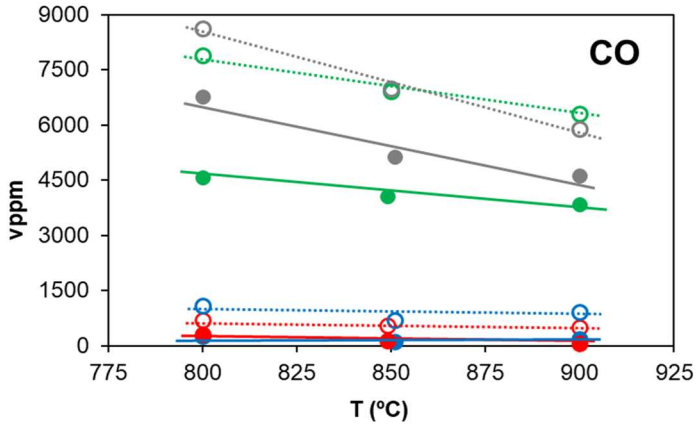
2nd experimental campaign CFB Combustion

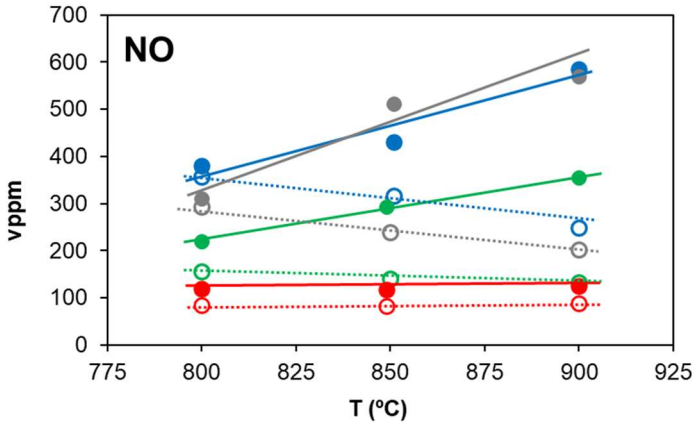
Comparative emissions under reference operating conditions (850 ºC, 20% air excess)

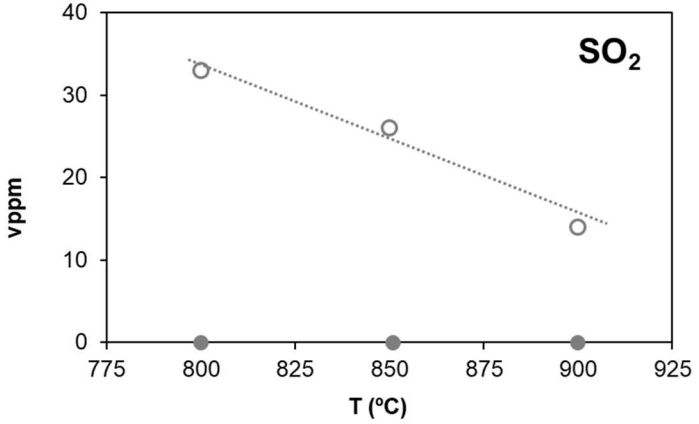
	CO_2 (%)	O_2 (%)	CO vppm	SO_2 vppm	NO vppm	NO_2 vppm	N_2O vppm	NH_3 mg/kg bio	Tars g/kg bio
Pine pellets	16.5	3.9	132	0	117	10	< 10	0	0.04
Olive stones	17.4	3.3	4047	0	293	10	< 10	0	0.74
Spruce chips	16.4	3.9	107	0	430	22	< 10	0	0.10
RDF	14.9	3.6	5130	<10	510	21	< 10	0	0.15

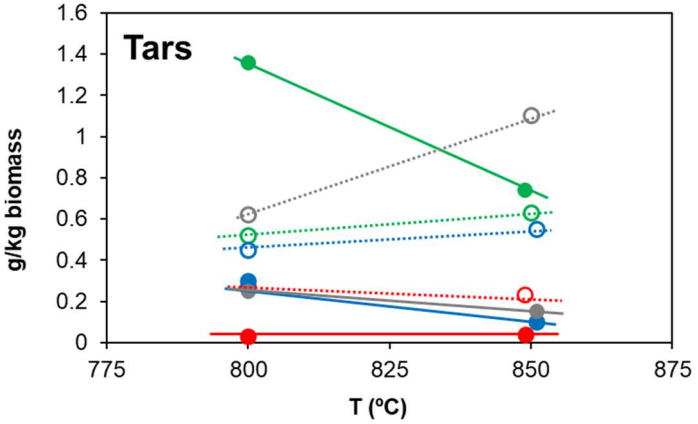
No agglomeration
Negligible ash-ilmenite interaction
No ash components accumulation

CFB Combustion: sand-ilmenite







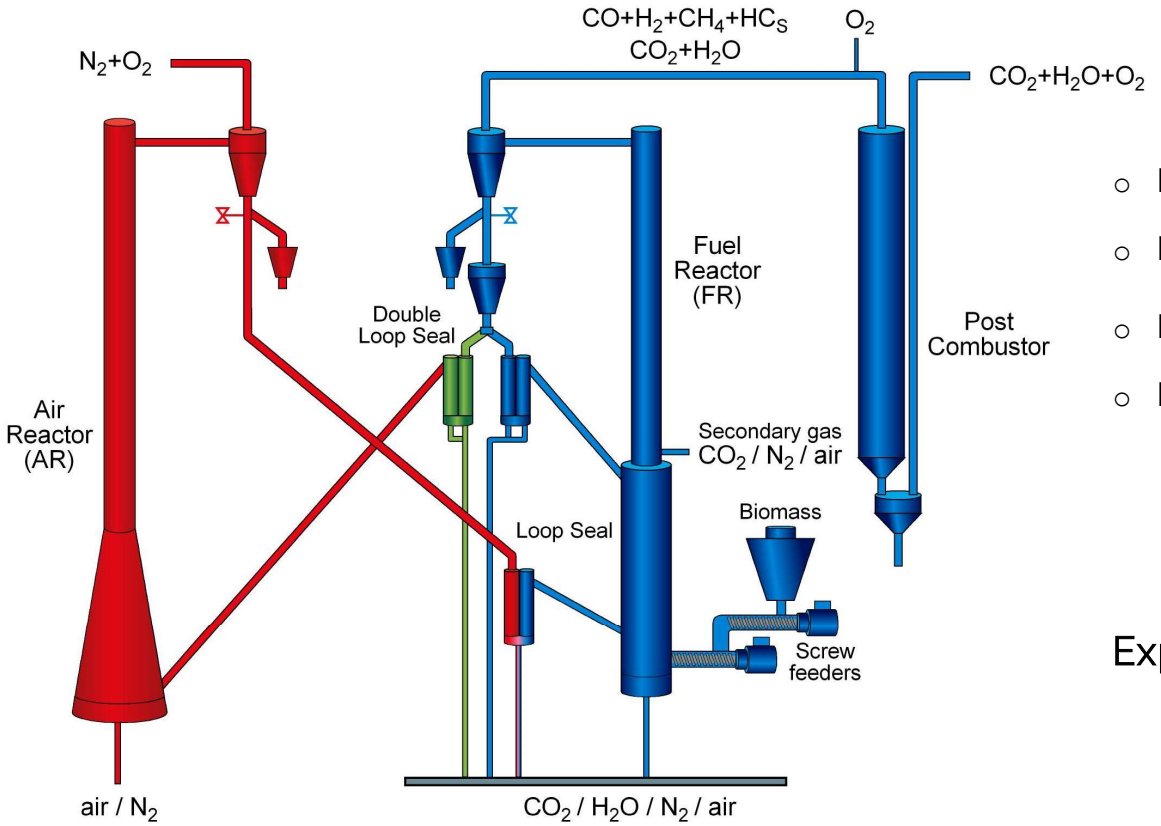


- Pine wood pellets
- Spruce chips
- Olive stone
- RDF
- Silica sand
- Ilmenite

Ilmenite yielded lower CO and significantly reduced tar emissions: oxygen polishing effect

NO higher with ilmenite: ilmenite as a catalyst (increasing with T)

3rd experimental campaign CLC

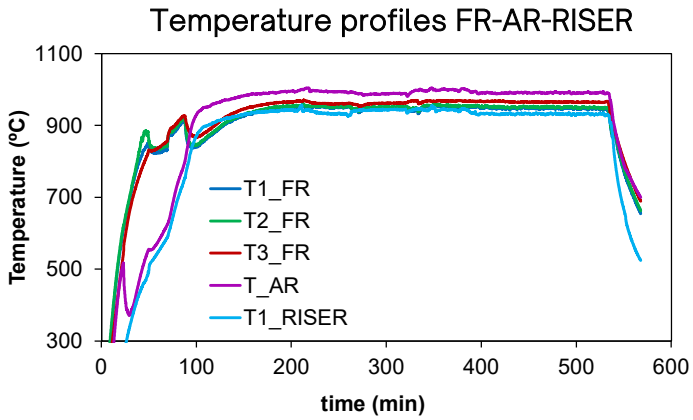


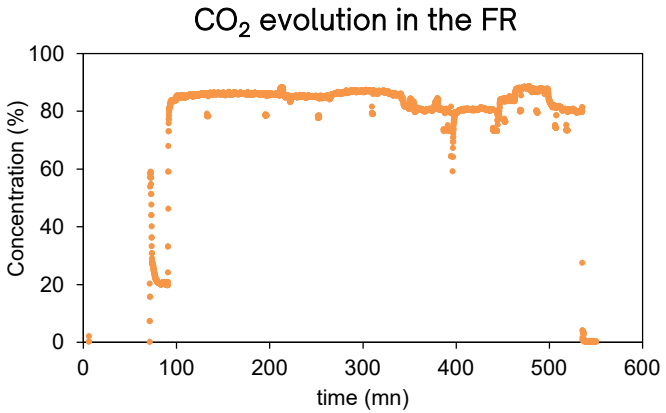
- Bed material: ILMENITE (dp = 100 – 300 μm)
- Post-oxidation chamber
- Fuel: PINE WOOD PELLETS & SPRUCE CHIPS
- Reference conditions:
  - FR temperature: 950 °C
  - Excess air: 20 %
  - FR superficial gas velocity: ~2.3 m/s (bottom), ~4.5 m/s (top)
  - AR superficial gas velocity: ~0.4 m/s (bottom), ~5.3 m/s (top)

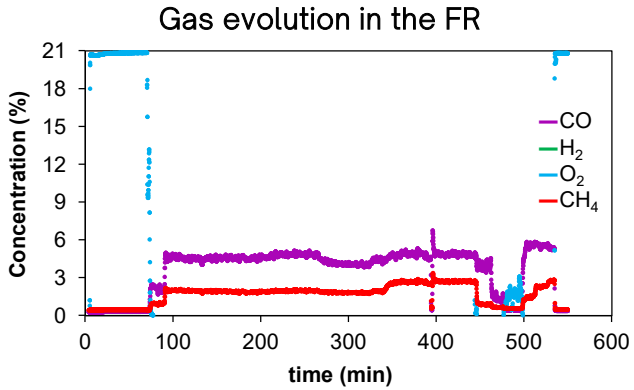
Experimental variables to be analyzed:

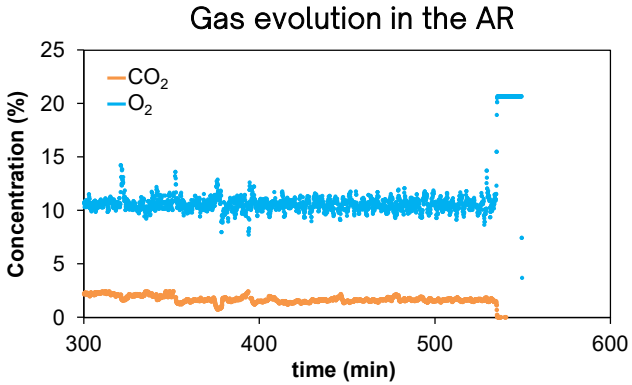
- Temperature: 850 – 950 ºC
- Φ (oxygen to fuel ratio): 1 – 2
- Post oxidation chamber behavior

3rd experimental campaign CLC (pine wood pellets & ilmenite)









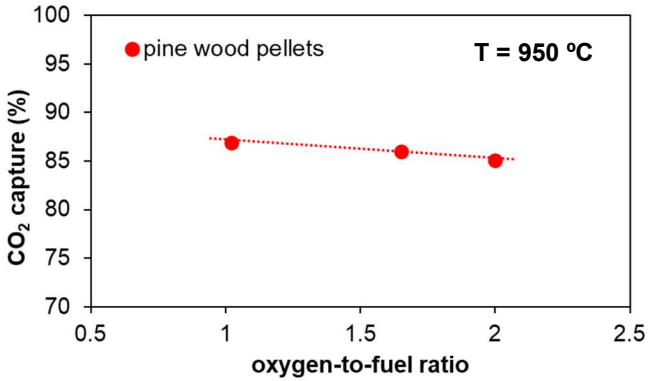
One day typical CLC experiment

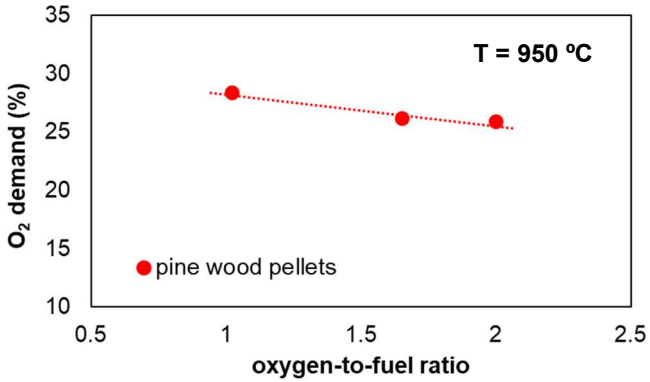
Smooth and steady state profiles

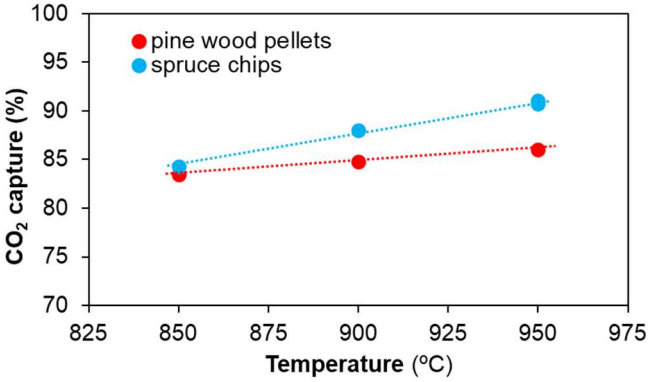
3rd experimental campaign CLC (pine wood pellets/spruce & ilmenite)

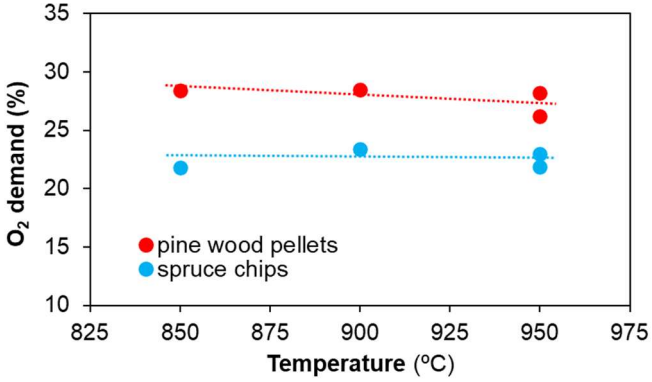
Thermal power ≈ 20 kW

Carbon conversion FR + AR > 98%









Oxygen carrier-to-fuel ratio (ϕ)

$$\frac{\text{Potential oxygen available in the oxygen carrier}}{\text{Oxygen demanded for the complete combustion of the fuel}}$$

CO_2 capture efficiency (η_{CC})

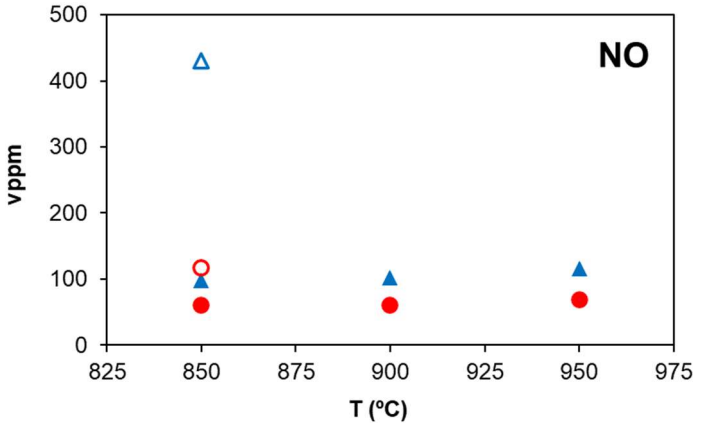
$$\frac{\text{Carbon from fuel in gases from the FR}}{\text{Carbon in the fuel fed}}$$

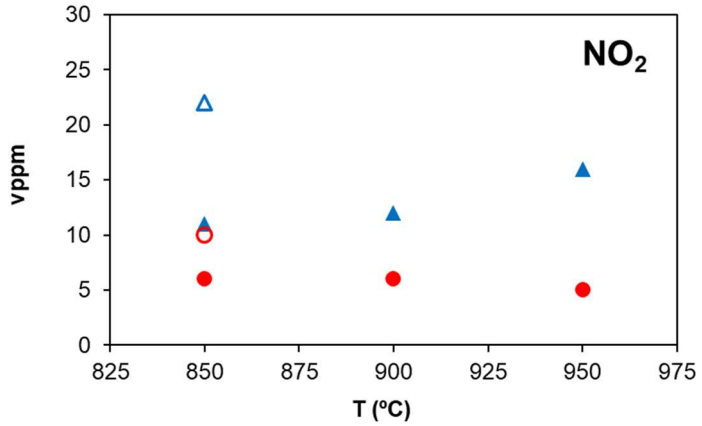
Total oxygen demand (Ω_{OD})

$$\frac{\text{Oxygen demanded for the complete combustion of gases (FR)}}{\text{Oxygen demanded for the complete combustion of the fuel}}$$

3rd experimental campaign CLC (pine wood pellets/spruce & ilmenite)

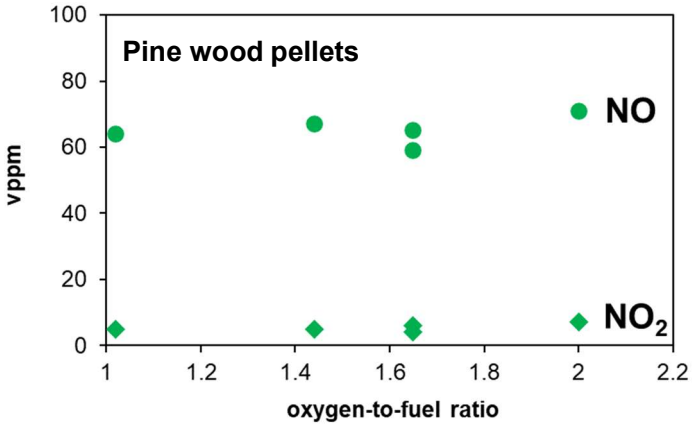
Lower NOx emissions for CLC operation mode





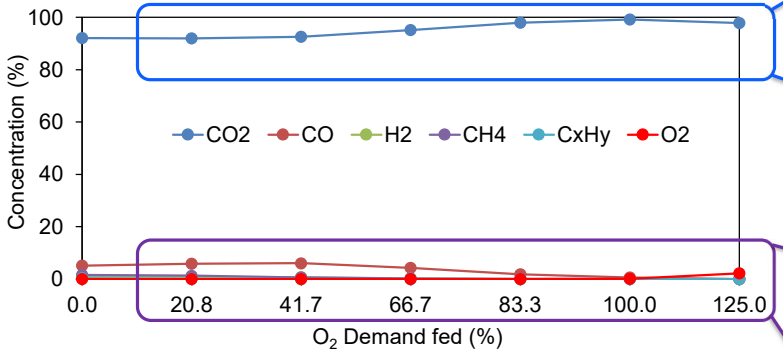
- Pine wood pellets (CLC)
- Pine wood pellets (CFB)
- Spruce chips (CLC)
- Spruce chips (CFB)

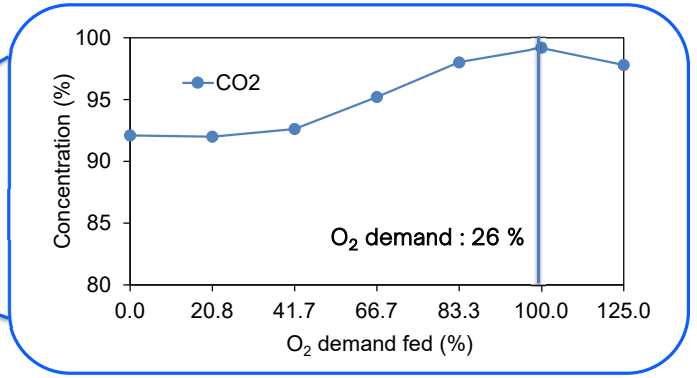
Little influence of oxygen to fuel ratio on NOx emissions

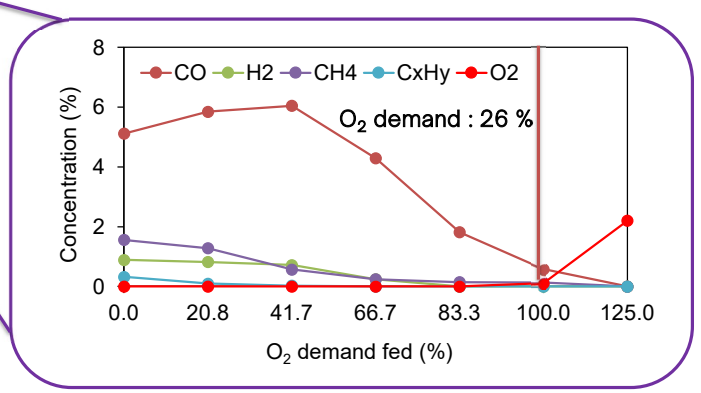


3rd experimental campaign CLC: Post Oxidation Chamber

Temperature: 950 ˚C
Oxygen to fuel ratio= 1.44
O_2 demand : 26 %
Fuel: Pine wood pellets





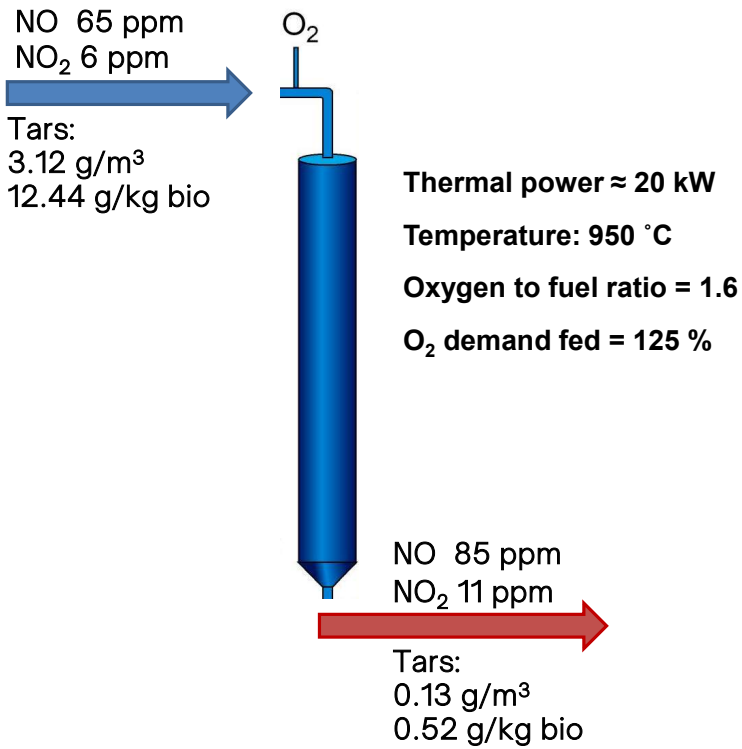


O_2 Demand fed %	0	100	125
CO_2	92.1	99.18	97.82
CO	5.12	0.58	<0.05
H_2	0.89	<0.05	<0.05
CH_4	1.56	0.13	<0.05
C_xH_y	0.32	<0.05	<0.05
O_2	0	0.11	2.2

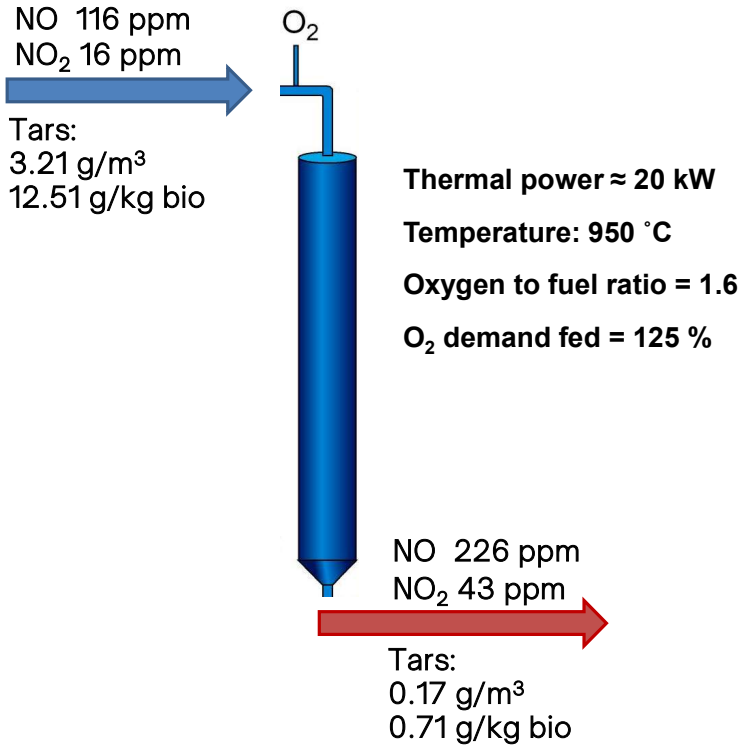


3rd experimental campaign CLC: Post Oxidation Chamber

PINE WOOD PELLETS

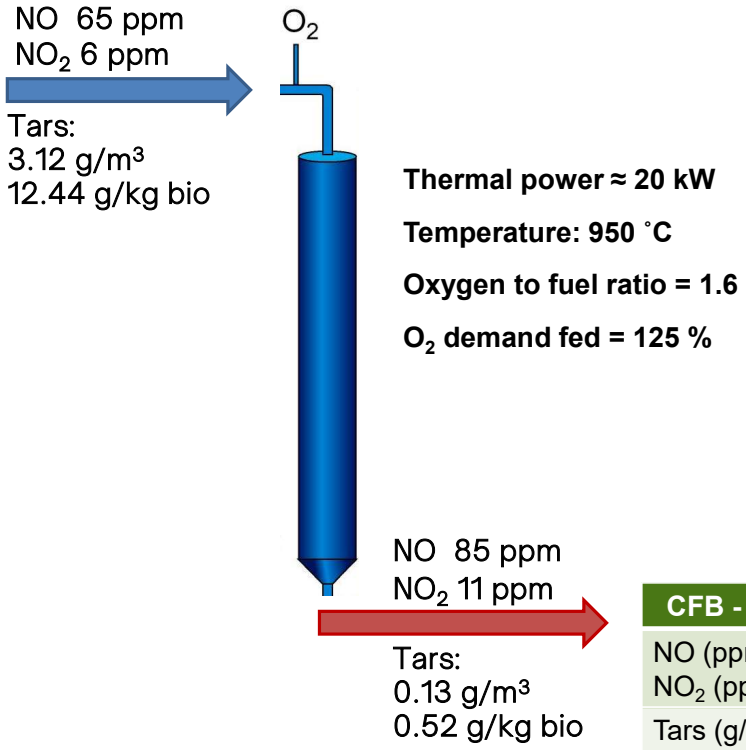


SPRUCE CHIPS



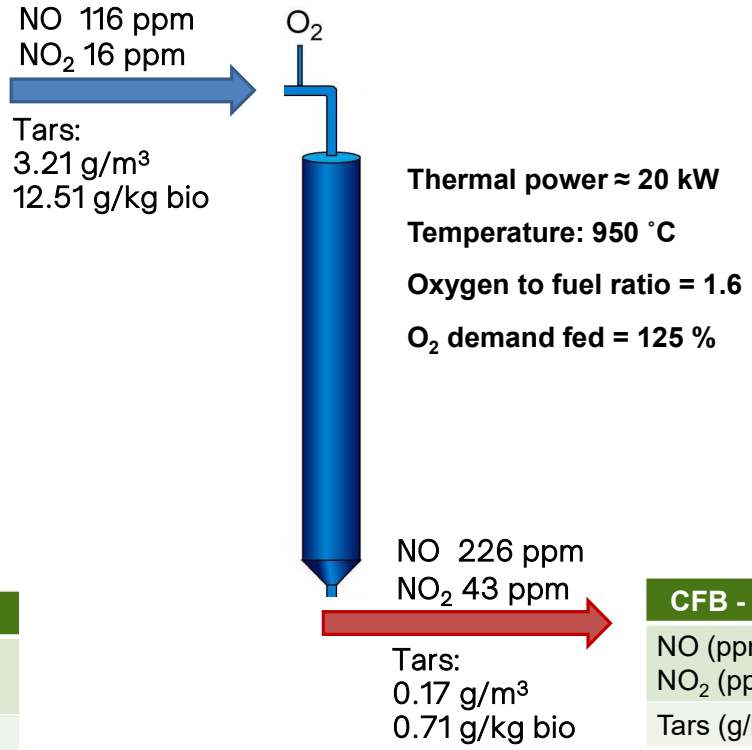
3rd experimental campaign CLC: Post Oxidation Chamber

PINE WOOD PELLETS



CFB - ilmenite experiments	
NO (ppmv) NO_2 (ppmv)	117 10
Tars (g/kg biomass)	0.04

SPRUCE CHIPS



CFB - ilmenite experiments	
NO (ppmv) NO_2 (ppmv)	430 22
Tars (g/kg biomass)	0.1

Conclusions

- **Flexible CFB-CLC operation** demonstrated the technical feasibility of converting biogenic residues into heat and power.
- Conventional **CFB combustion tests:**
  - Stable operation achieving **combustion efficiencies above 98%.**
  - **Agglomeration** was observed when using silica sand as bed material and olive stone as fuel.
  - **No agglomeration** when **ilmenite** was used as bed material.
- **CLC experiments** using ilmenite as the oxygen carrier and pine wood pellets as fuel:
  - Stable operation, with **carbon conversion exceeding 98%.**
  - **Post-oxidation chamber** ensures the **complete oxidation of unburned gaseous compounds** and improve overall process performance.

Ongoing work

Expand the CLC experimental campaign to the rest of the biomass (spruce chips, olive stones, RDF)

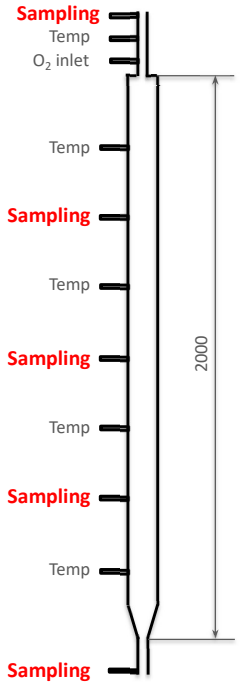


Use of packings: strategy to enhance fuel conversion





Post Oxidation Chamber sampling profiles





Questions / Comments

Please follow our project website and our LinkedIn page for the latest news and developments.
Website: https://www.bioflexclcproject.eu/
LinkedIn: https://www.linkedin.com/company/bio-flexclc/

Website

LinkedIn

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