Role of ash chemistry in

CHEMICAL LOOPING WITH BIOMASS

virtual seminar to bring together big ideas

MAY | 25-26 | 2021

9:00AM-12:30PM (CET,GMT+2)

CHALMERS UNIVERSITY OF TECHNOLOGY

Vetenskapsrådet Swedish Research Council

CSIC expertise on Biomass Chemical Looping Gasification (BCLG)

Francisco García-Labiano

glabiano@icb.csic.es

Instituto de Carboquímica (ICB), Zaragoza, Spain

Consejo Superior de Investigaciones Científicas (CSIC)

GOBIERNO DE ESPAÑA | MINISTERIO DE CIENCIA E INNOVACIÓN

CSIC Consejo Superior de Investigaciones Científicas

icb INSTITUTO DE CARBOQUIMICA

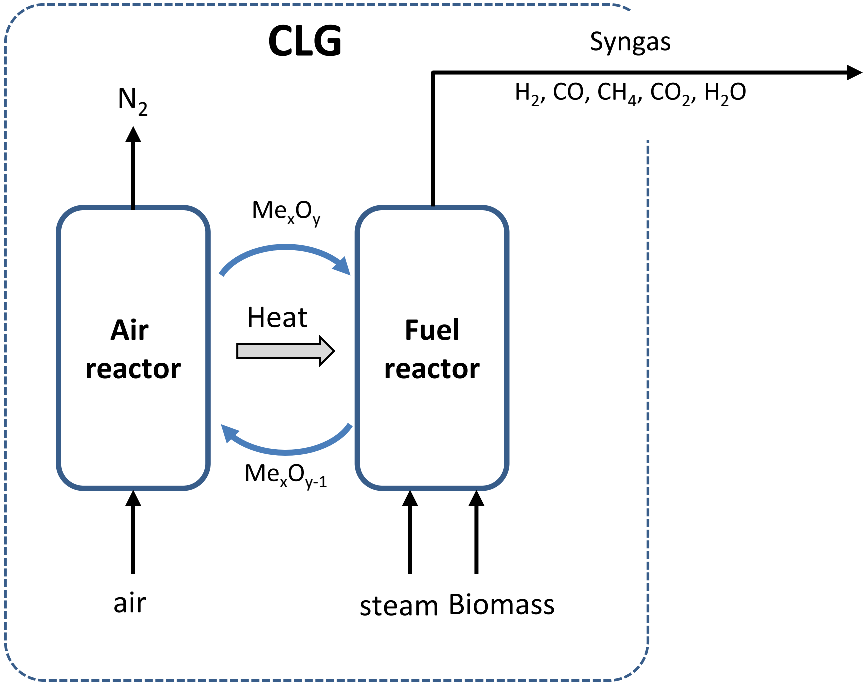
May 25-26, 2021

Outline

- General CLG concept
- Control of oxygen in BCLG.
- Summary of BCLG tests at CSIC
- Experience in the 50 kW_{th} CLG unit regarding agglomeration

Chemical Looping Gasification

Biomass, wastes



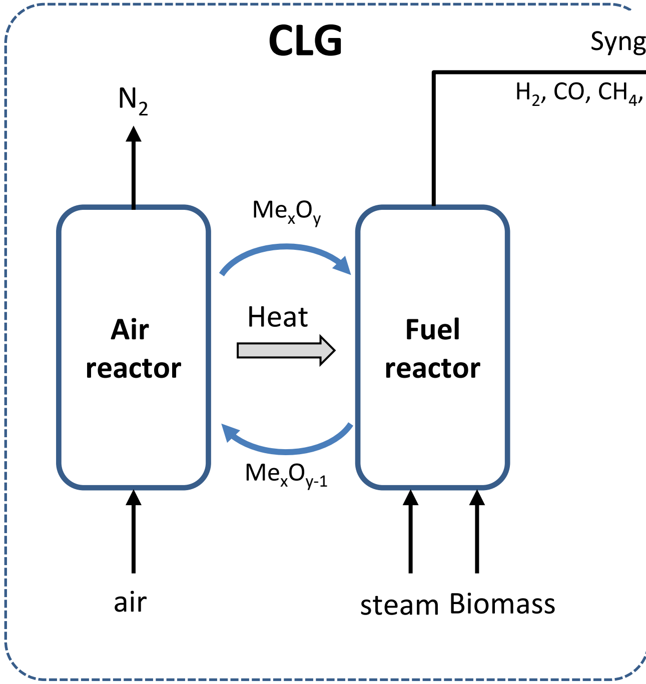
SYNGAS

H_2
FT-diesel, gasoline
Methanol
DME, MTBE
chemicals

- Pure syngas stream (no N_2 dilution and without using ASU unit)
- Autothermic
- Less steam consumption than conventional gasification processes
- Low tar generation (catalytic cproperties of the Me_xO_y)
- Less emission of CO_2 to the atmosphere (CO_2 concentrated in syngas)
- Less corrosion in heat exchangers (located in AR)

Chemical Looping Gasification

Biomass, wastes



SYNGAS

H_2
FT-diesel, gasoline
Methanol
DME, MTBE
chemicals

Oxygen-to-biomass ratio, λ

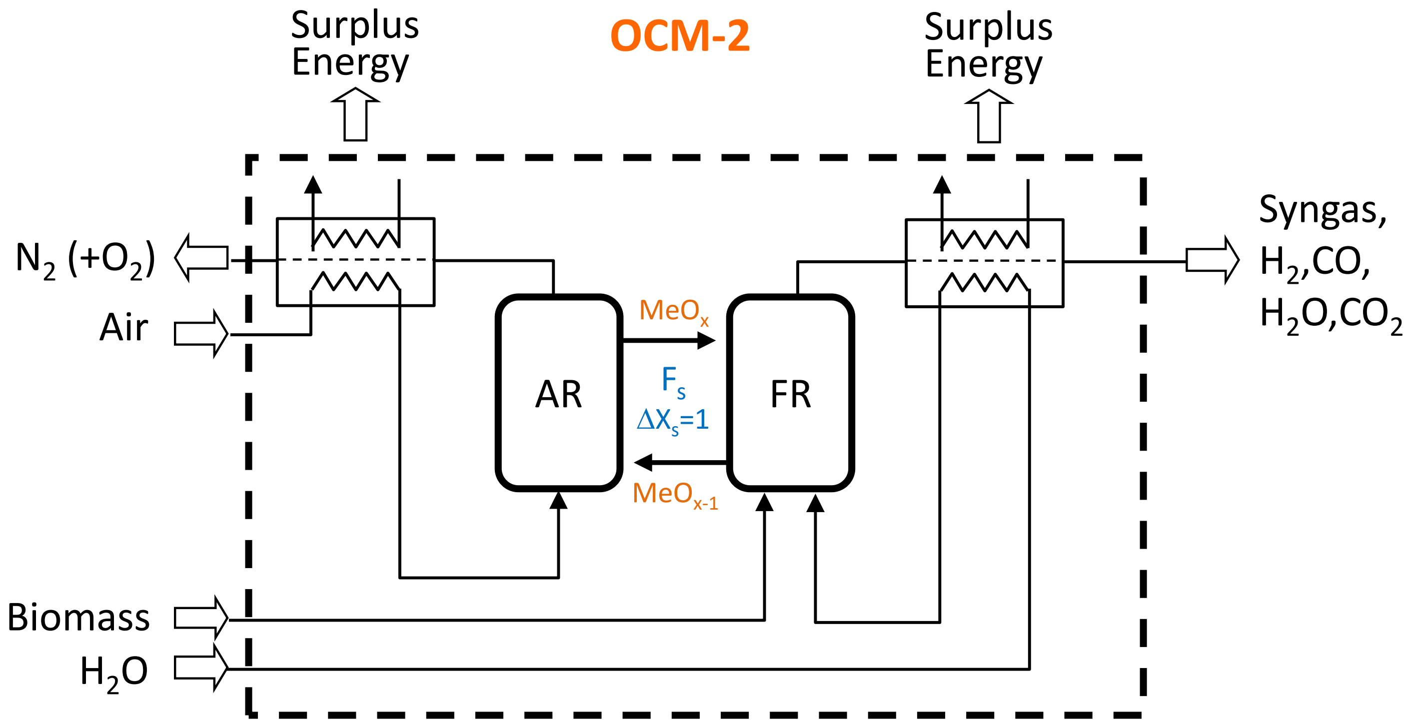
$$\lambda = \frac{\text{oxygen fed in the AR (mol/h)}}{\text{oxygen needed for full biomass combustion (mol/h)}}$$

Steam to Biomass ratio, S/B

$$S/B = \frac{\text{flow of steam (kg/h)}}{\text{flow of dry biomass (kg/h)}}$$

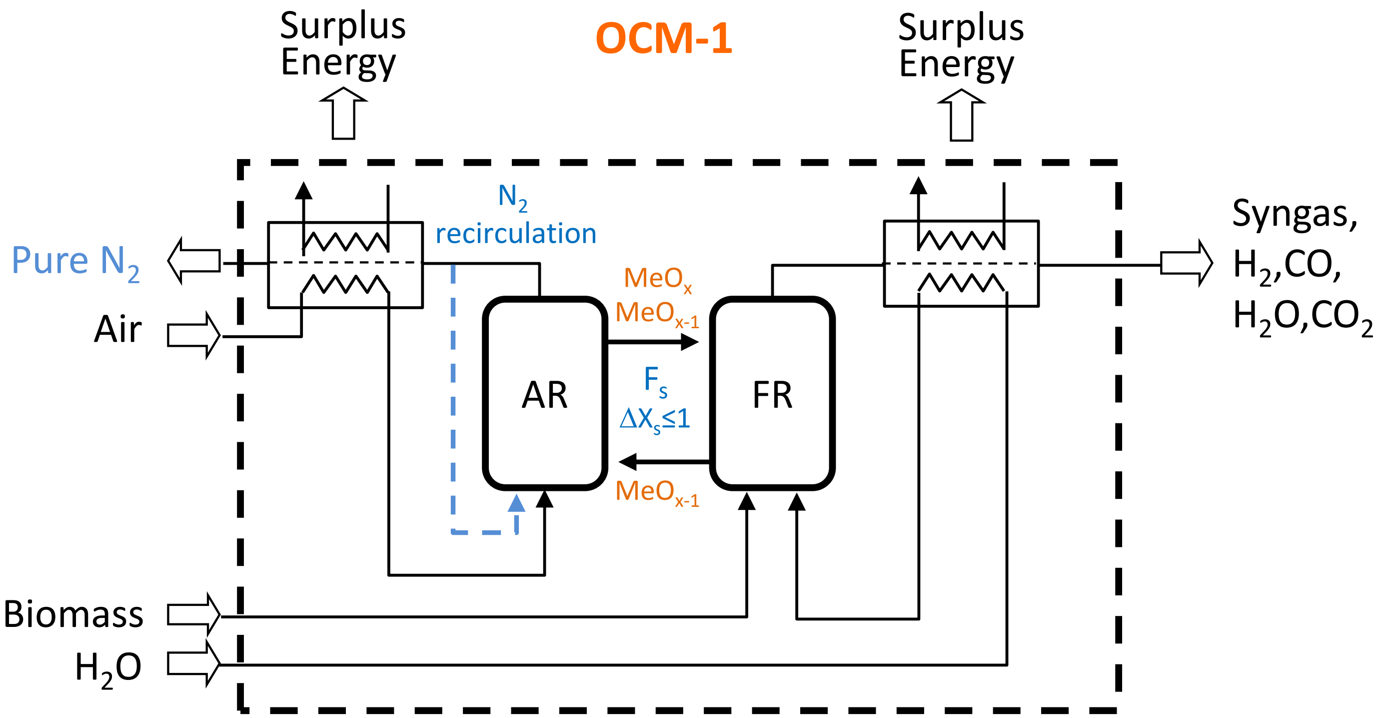
Temperature, T

Control of the oxygen in BCLG



- Controlled by the oxygen carrier circulation flow.
- The OC circulation flow is fixed for a given oxygen-to-biomass ratio, λ
- The air-to-biomass ratio is higher to the oxygen-to-biomass ratio, λ

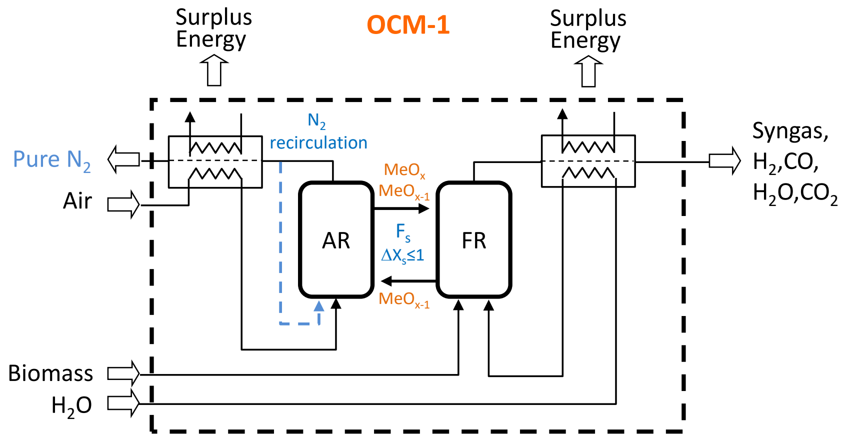
Control of the oxygen in BCLG

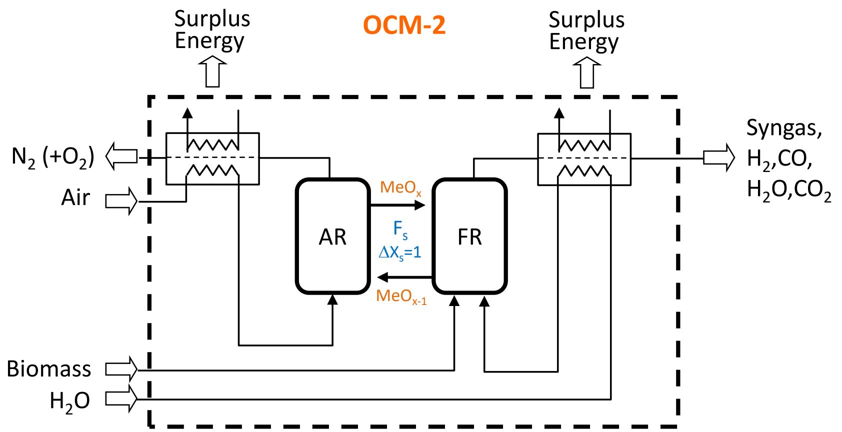


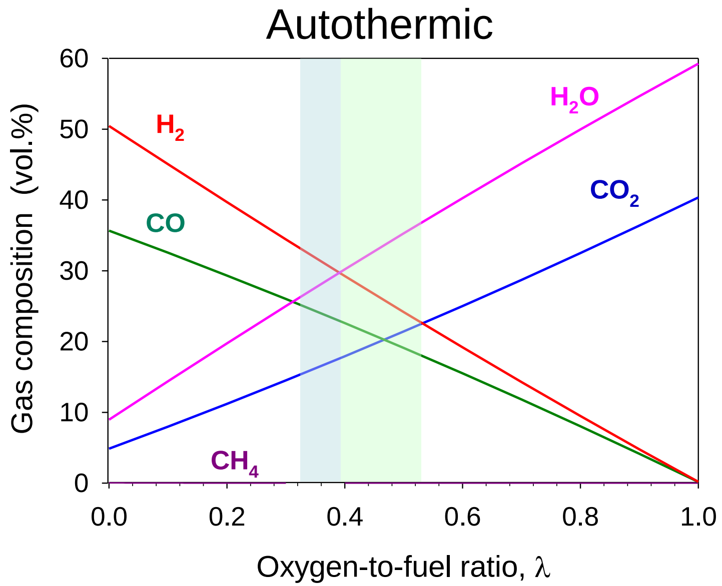
- Controlling the air-to-biomass ratio.
- Oxygen lattice transferred, λ, does not depend on the OC circulation flow
- Pure N_2 is obtained at the AR outlet

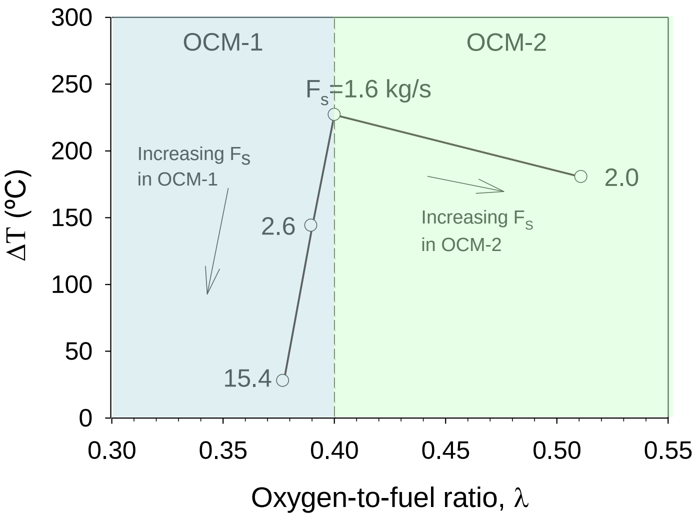
Control of the oxygen in BCLG

OCM-1 is preferred than OCM-2



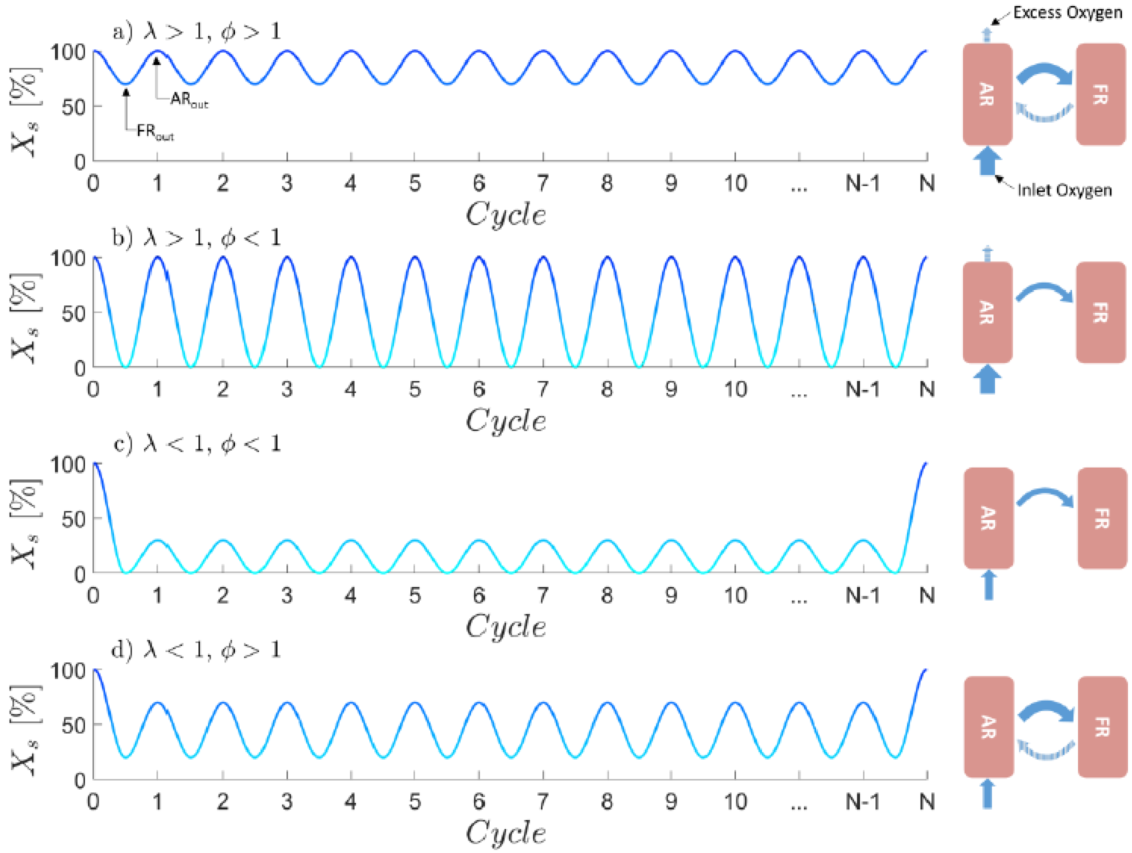






Samprón et al. Energy 226, 2021, 120317

Lines correspond to autothermal conditions



CLC

CLC

OC- Low oxygen transport capacity

CLG (OCM-1)

Limited O_2 in AR.

Low circulation rate

CLG (OCM-1)

Limited O_2 in AR

High circulation rate

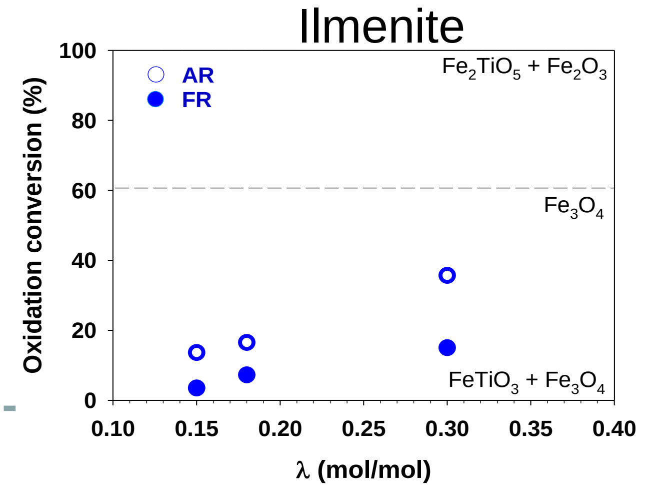
Figure 3. Different chemical looping modes (a–d) dependent on the air-to-fuel equivalence ratio λ and the oxygen-carrier-to-fuel equivalence ratio ϕ.

Oxygen carrier is highly reduced in FR and AR (OCM-1)

Dieringer et al. Appl. Sci. 2020, 10, 4271

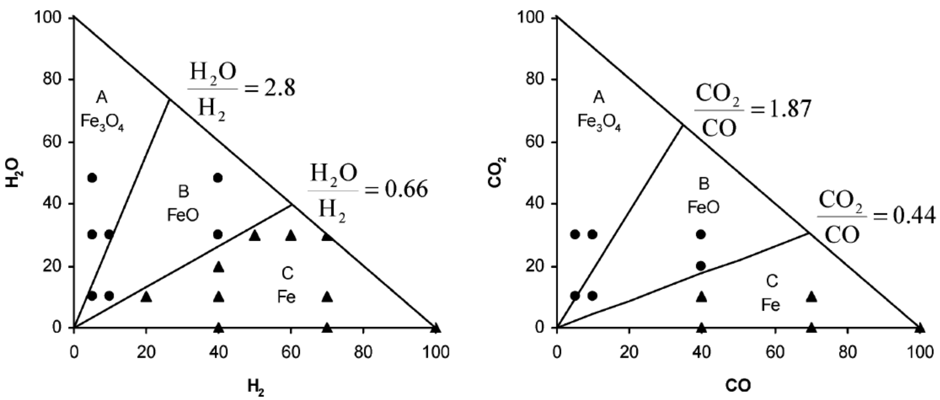
Redox pairs in BCLG

Mn-based	Fe-based	Ilmenite	Fe-Al synthetic
Mn_2O_3	Fe_2O_3	Fe_2TiO_5	$Fe_2O_3.\ Al_2O_3$
Mn_3O_4	Fe_3O_4		
MnO	FeO	$FeTiO_3$	$FeAl_2O_4$
Mn	Fe	Fe. TiO_2	Fe. Al_2O_3



Condori et al. Chem.Eng. J. 405, 2021, 126679

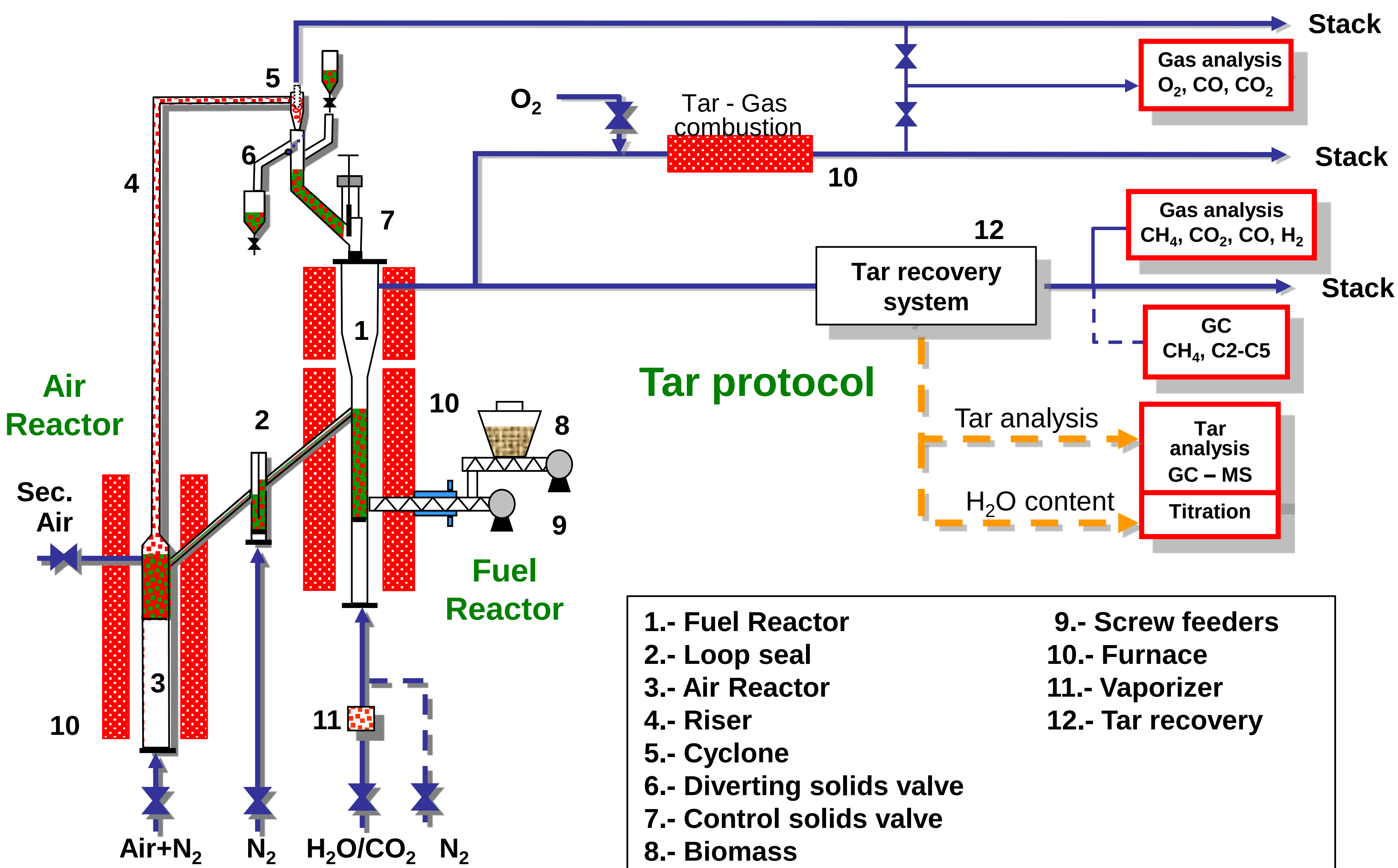
Thermodynamic data



Abad et al. Energy Fuels 21, 2007, 1843-1853.

Oxygen carrier
is highly reduced
in FR and AR (OCM-1)

1.5 kW_{th} CLG unit at ICB-CSIC



1.- Fuel Reactor
2.- Loop seal
3.- Air Reactor
4.- Riser
5.- Cyclone
6.- Diverting solids valve
7.- Control solids valve
8.- Biomass
9.- Screw feeders
10.- Furnace
11.- Vaporizer
12.- Tar recovery

Summary of operating conditions at ICB-CSIC.

Unit	Oxygen carrier	Biomass	Temperature ºC	Steam-to-fuel ratio $kg/kg_{drybiomass}$	Oxygen-to-fuel ratio (λ) mol/mol	Gasification time at steady state h
1.5 kW_{th}	Ilmenite	IWP	820 - 940	0 - 0.9	0.15 - 0.35	55
	Fe ore	IWP	820 - 940	0 – 0.6	0.15 – 0.5	40
	LD slag	IWP, almond shells, olive stone	820 - 940	0 – 0.6	0.15 – 0.5	60
	Mn ore	IWP	820 - 940	0 – 0.6	0.15 – 0.5	50
	Fe10Al	Pine wood	820 - 940	0 – 0.6	0.2 – 0.4	34
	Fe20Al	Pine wood	820 - 940	0 – 0.6	0.2 – 0.6	38
	Fe25Al	Pine wood	820 - 940	0 – 0.6	0.2 – 0.4	31
50 kW_{th}	Ilmenite	Wheat Straw pellets with additives	820 -990	0.7	0.2 - 0.4	37

- >300 h of CLG operation under steady state conditions.
- No agglomeration observed in spite of the high reduction level of the OC

Summary of biomasses used at ICB-CSIC

Industrial wood pellets

Pine wood

Olive Stone

Almond Shell

Wheat straw pellets + additives

Woody biomass

Herbaceous or agricultural straw

S.V. Vassilev et al. / Fuel 89 (2010) 913–933 931

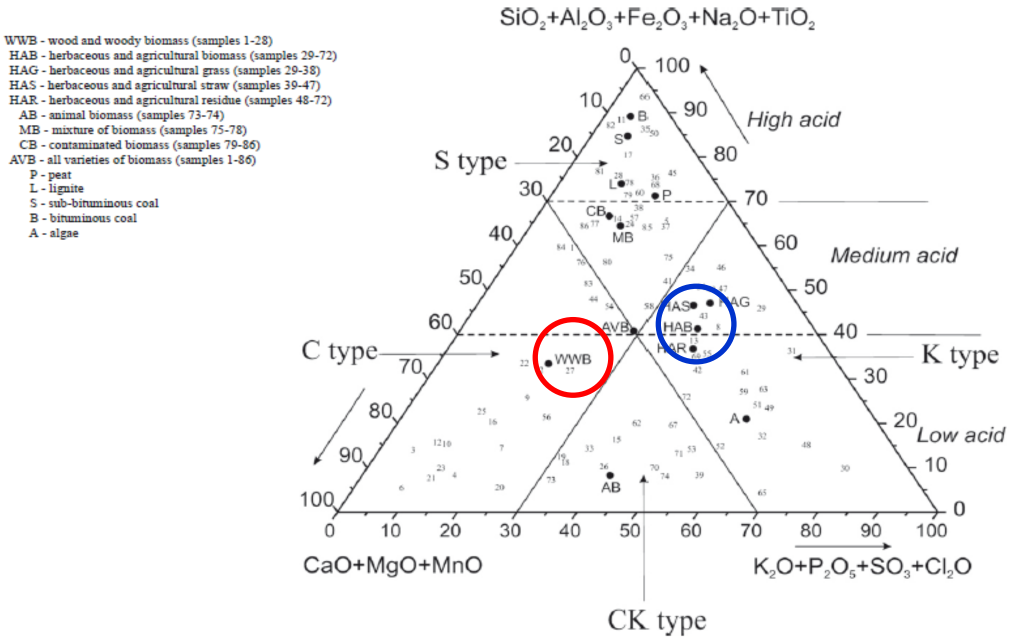
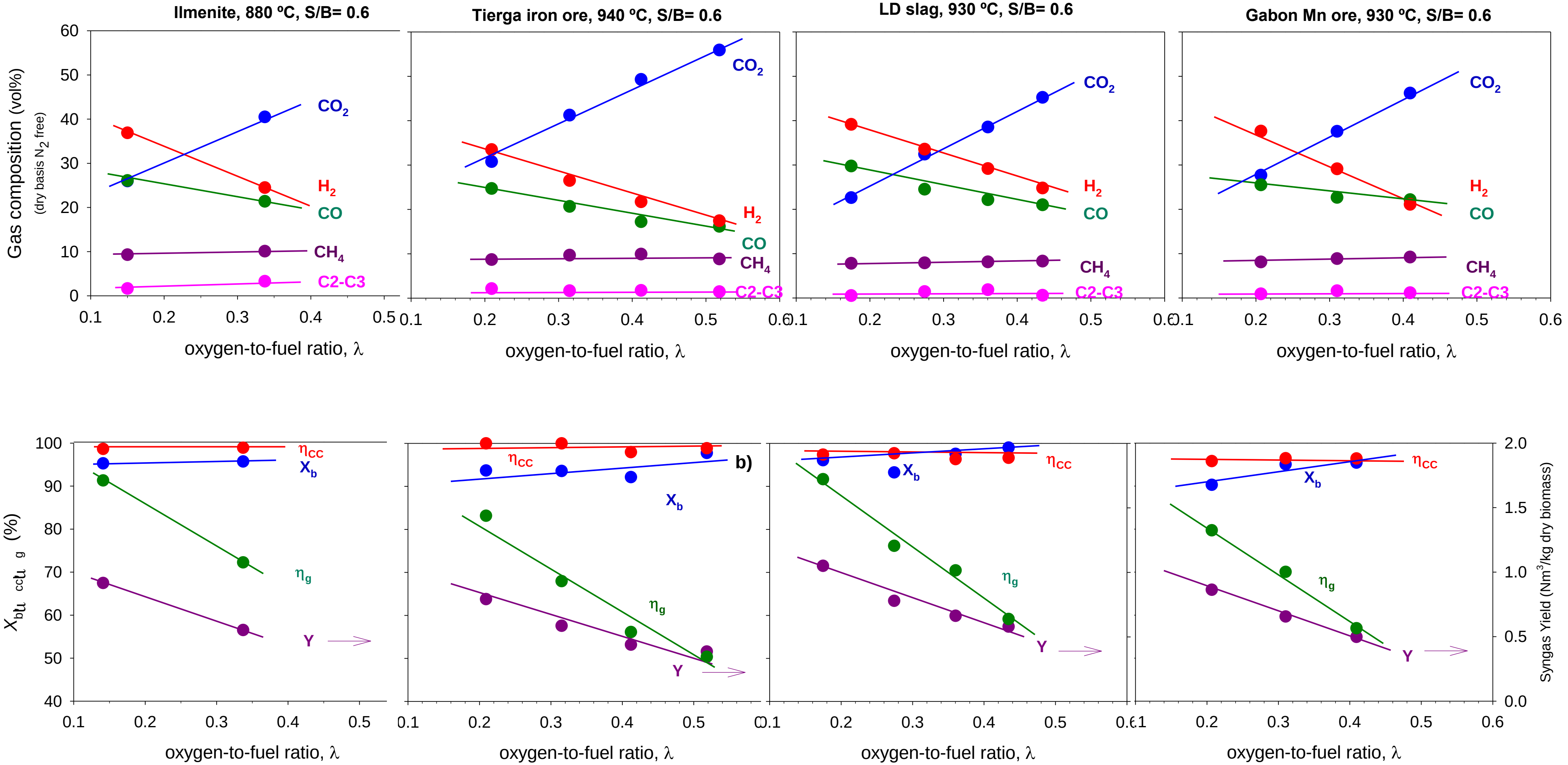
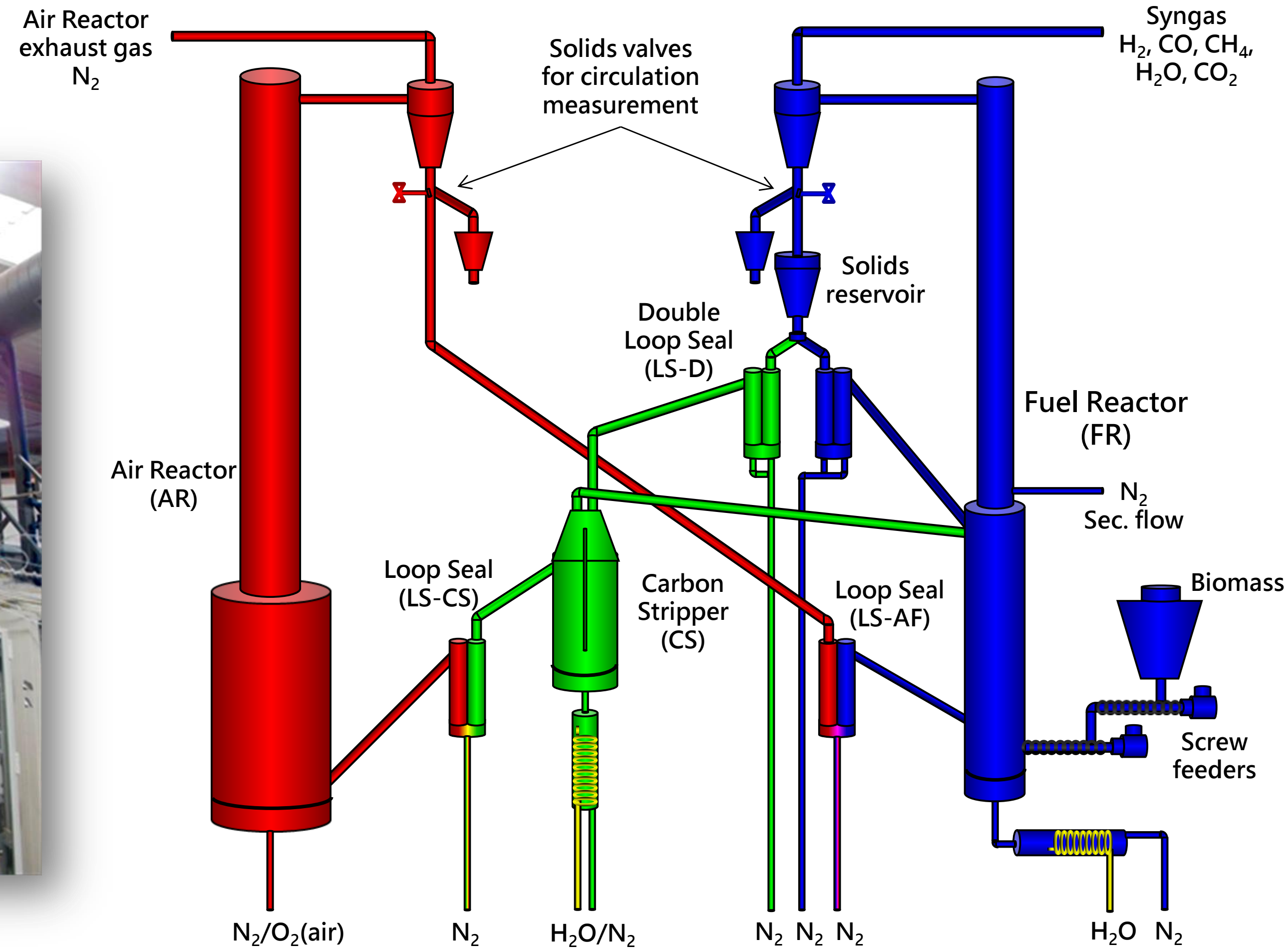


Fig. 4. Chemical classification system of the inorganic matter in high-temperature biomass ashes based on 78 varieties of biomass, wt.%

Ilmenite Tierga Fe ore LD slag Gabon Mn ore



50 kW_{th} Chemical Looping Gasification unit at CSIC



Control of the process by limiting the oxygen fed in Air Reactor

Oxygen-carrier

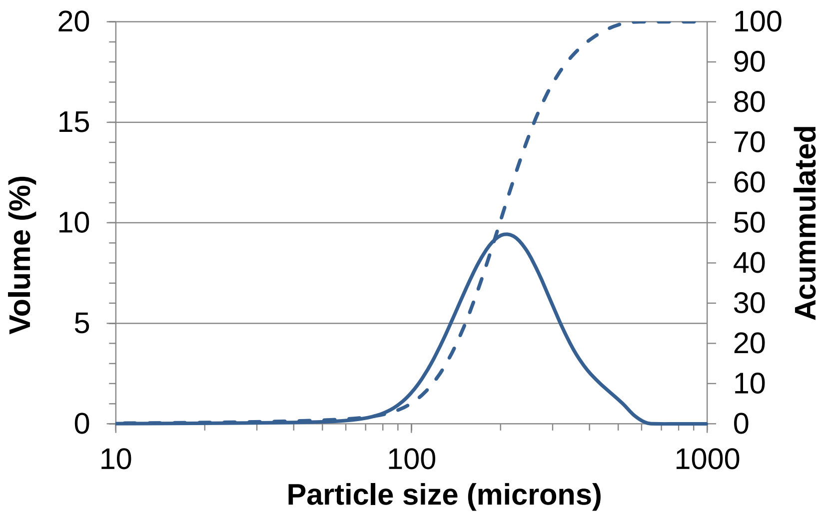
ILMENITE

active phases		
Oxidized		**Reduced**
Fe_2TiO_5	⟷	$FeTiO_3$
Fe_2O_3	⟷	Fe_3O_4

Fresh ilmenite from Titania, Norway:
Calcination: 950 ºC in air for 2 h
Circulated 6 h at 800 ºC in air

Calcined ilmenite

Fe_2TiO_5	54.7 wt.%
Fe_2O_3	11.2 wt.%
TiO_2	28.6 wt.%
Inerts	5.5 wt.%



Mean µm	10% µm	25% µm	50% µm	75% µm	90% µm
224	<123	<159	<209	<273	<353

PROPERTIES	Calcined ilmenite
Particle size (µm)	100-300
True density (kg/m^3)	4100
$R_{O,ilm}$ (%)	4.0
Porosity (%)	1.2
Crushing strength(N)	2.2
XRD (main species)	Fe_2TiO_5, Fe_2O_3, TiO_2

Fuel

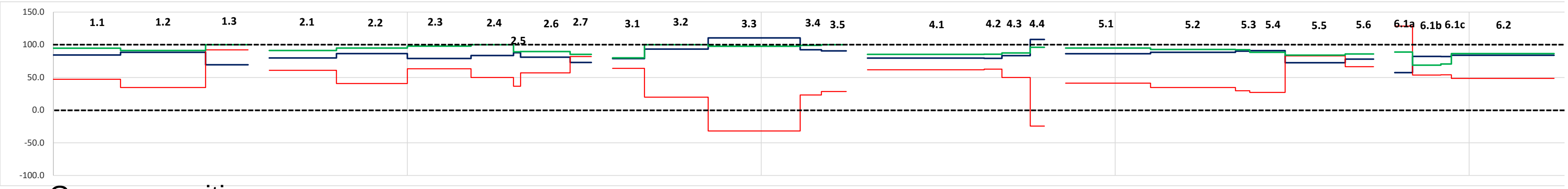
Wheat Straw with additives – CENER-

Proximate analysis		
Moisture content	wt.%; wb	10.3
Ash content	wt.%; db	7.0
Volatile matter	wt.%; db	77.7
Fixed carbon(1)	wt.%; db	15.3
Ultimate analysis		
C	wt.%; db	46.1
	wt.%; daf	49.6
H	wt.%; db	5.8
	wt.%; daf	6.2
N	wt.%; db	0.39
	wt.%; daf	0.42
S	wt.%; db	0.105
	wt.%; daf	0.113
Cl	wt.%; db	0.100
	wt.%; daf	0.108
Net calorific value		
NCV	MJ/kg; db	17.2
	MJ/kg; daf	18.5

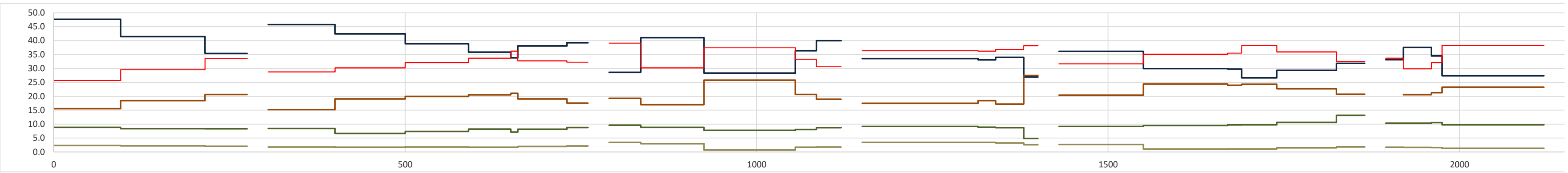
Major elemental ash composition in additive wheat straw pellets

Al	mg/kg (w/w)	158
Ca	mg/kg (w/w)	11,500
Fe	mg/kg (w/w)	172
K	mg/kg (w/w)	7,330
Mg	mg/kg (w/w)	982
Na	mg/kg (w/w)	186
P	mg/kg (w/w)	448
Si	mg/kg (w/w)	10,200
Ti	mg/kg (w/w)	10

Relevant efficiency parameters



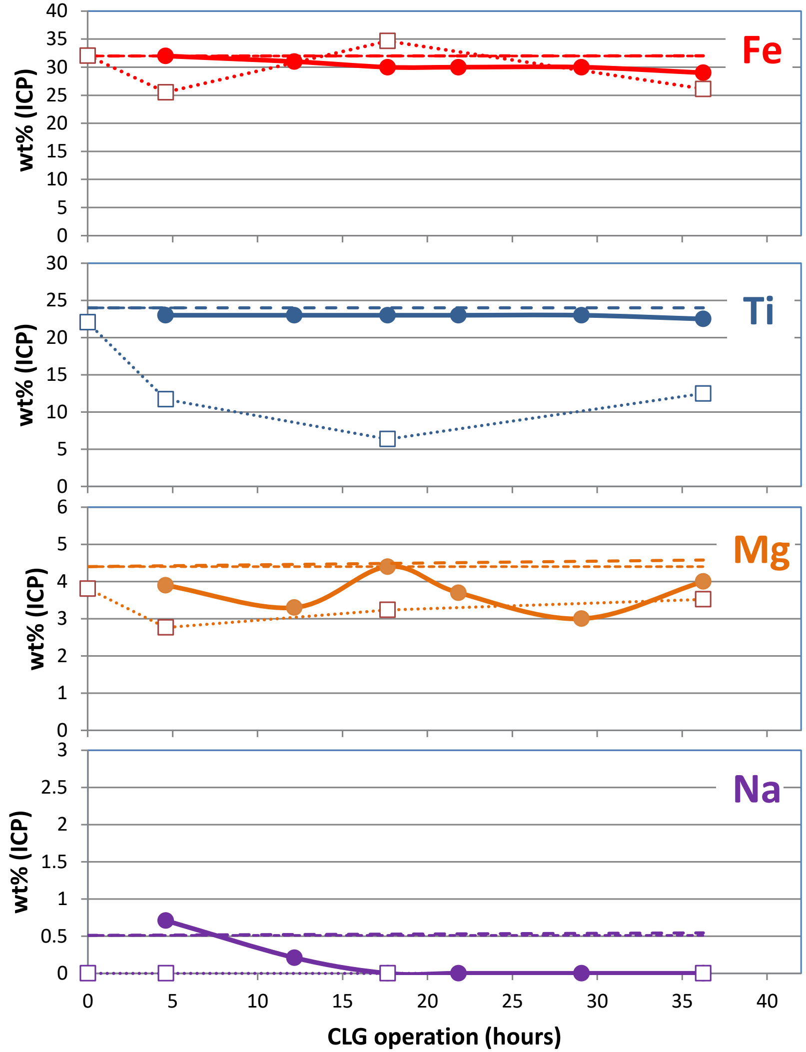
Gas composition



Main Achievements

- 6 days CLG. 37 h of continuous CLG operation
- 18 kW_t (4 kg/h of biomass)
- Smooth operation
- Several operating conditions analyzed
    - Temperature, T= 800 - 980 ºC
    - Oxygen to fuel ratio, λ= 0.13 - 0.4
    - Steam to biomass ratio, S/B= 0.7
- Tar recovery
- **Agglomeration analyzed**

Evolution of components (ICP)

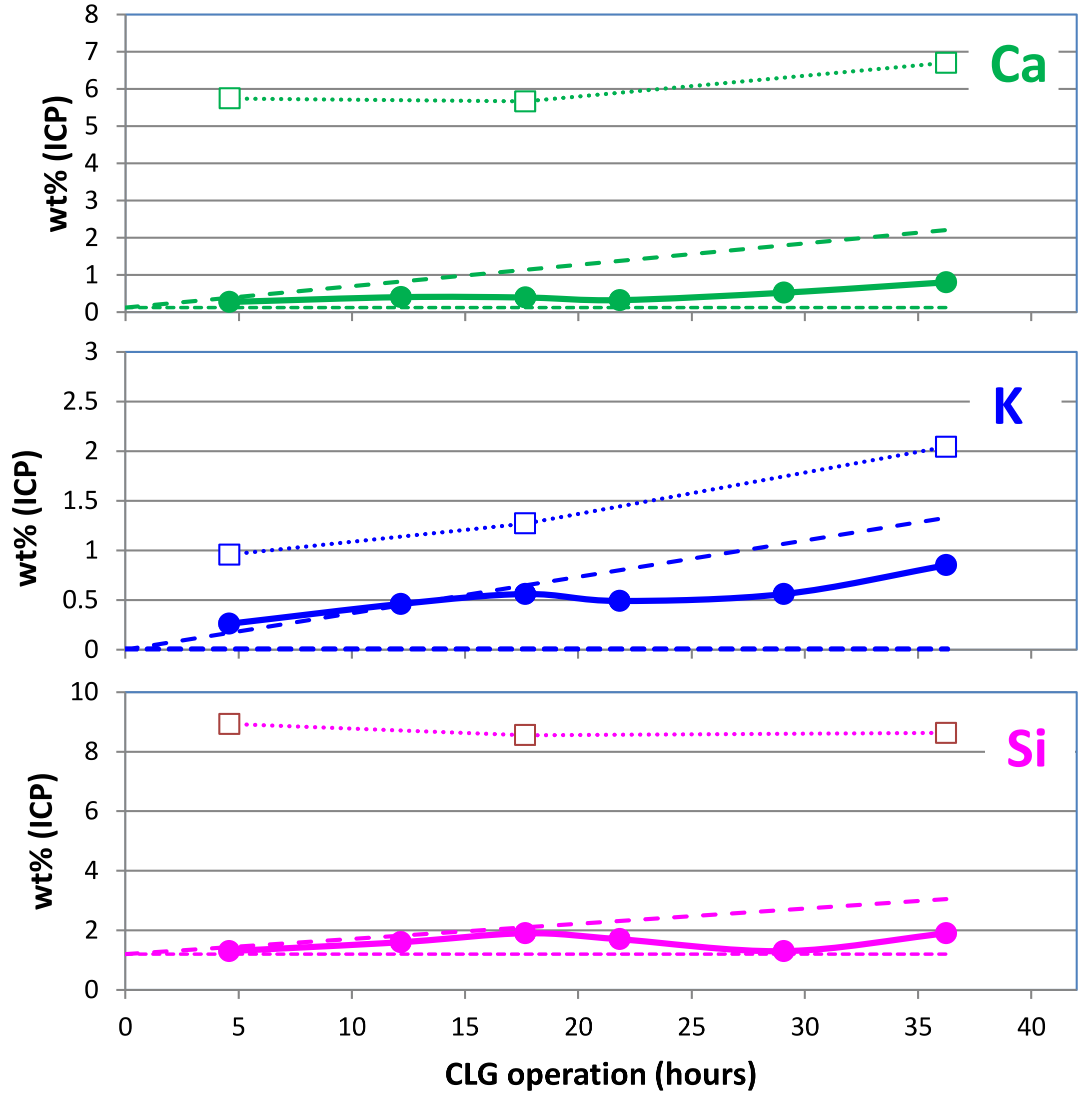


Major elemental ash composition in additive wheat straw pellets

Al	mg/kg b (w/w)	158
Ca	mg/kg b (w/w)	11,500
Fe	mg/kg b (w/w)	172
K	mg/kg b (w/w)	7,330
Mg	mg/kg b (w/w)	982
Na	mg/kg b (w/w)	186
P	mg/kg b (w/w)	448
Si	mg/kg b (w/w)	10,200
Ti	mg/kg b (w/w)	10

Dot line: already present in Ilmenite
Discontinuous line: ILM + fed in biomass
Dots: ICP content in OC
Square: ICP content in AR fines

80 kg oxygen carrier
145 kg biomass
37 hours CLG



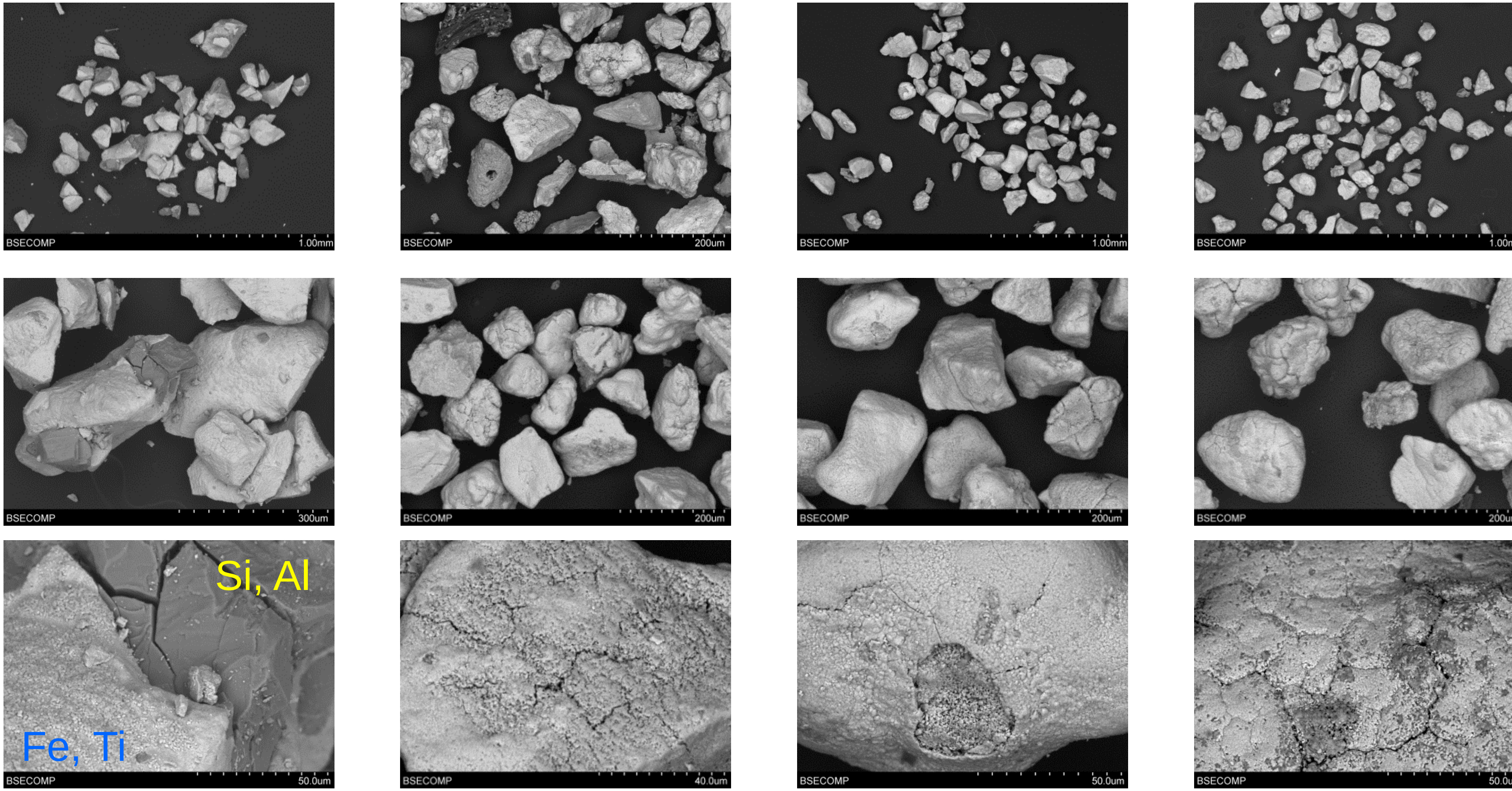
45% retained OC

65% retained OC

50% retained OC

Dot line: already present in Ilmenite
Discontinuous line: ILM + fed in biomass
Dots: ICP content in OC
Square: ICP content in AR fines

Calcined | Day 1 CLG | Day 3 CLG | Day 6 CLG



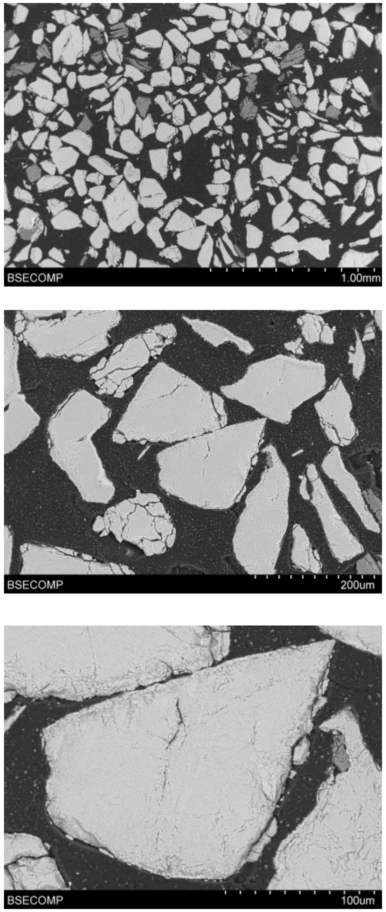
Calcined:
Particles with edges
Fines sticked
White particles: Fe, Ti
Black particles: Si, Al

Day 1 CLG:
Rounded particles
Some cracks

Day 3 CLG:
Some particles with detached shell

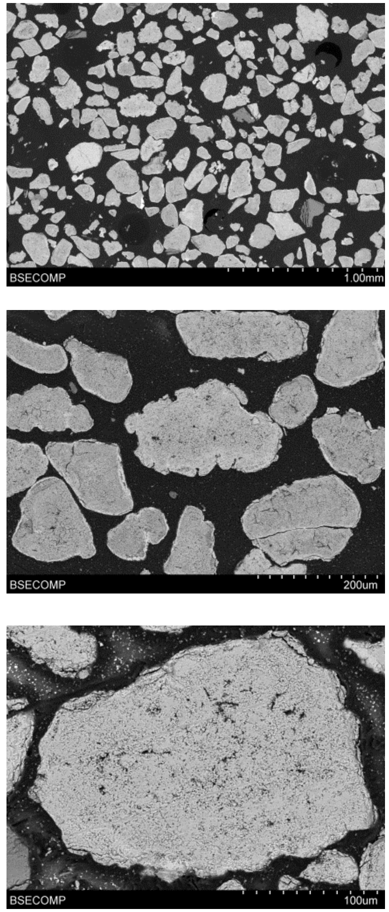
Day 6 CLG:
Good appearance
No agglomeration

Calcined



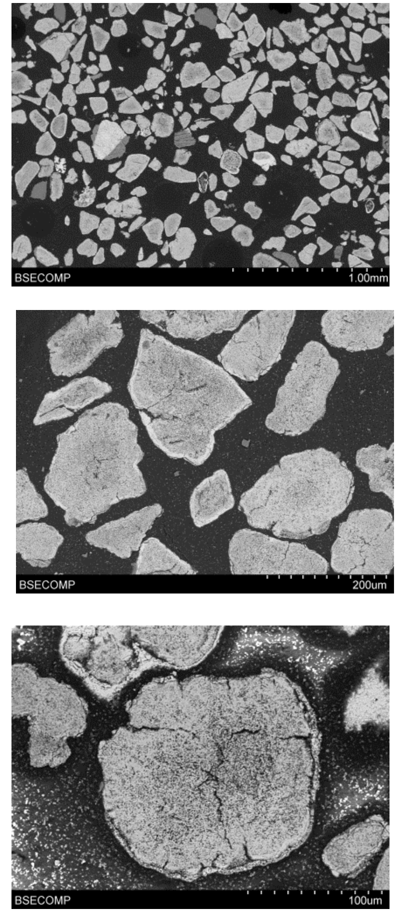
Particles with edges
Some internal cracks

Day 1 CLG



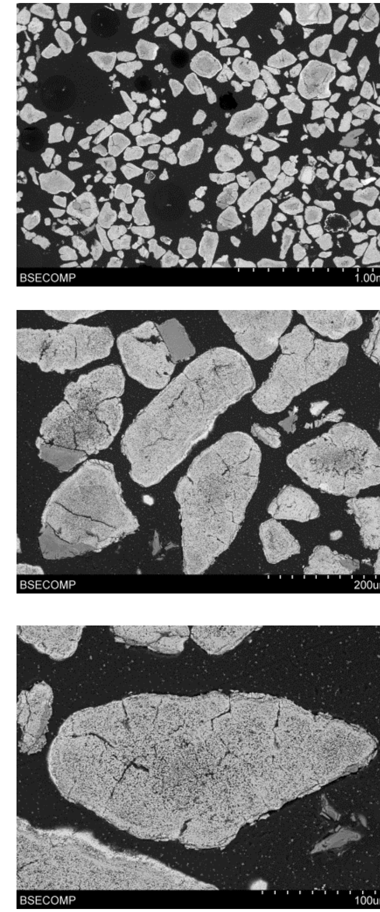
Rounded particles
White and black particles
External layer

Day 3 CLG



External layer
Some internal cracks

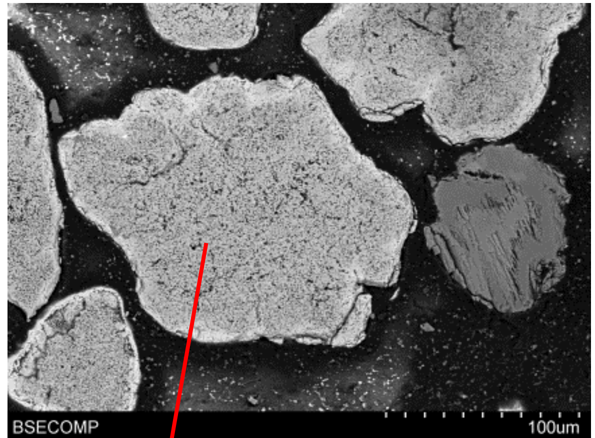
Day 6 CLG

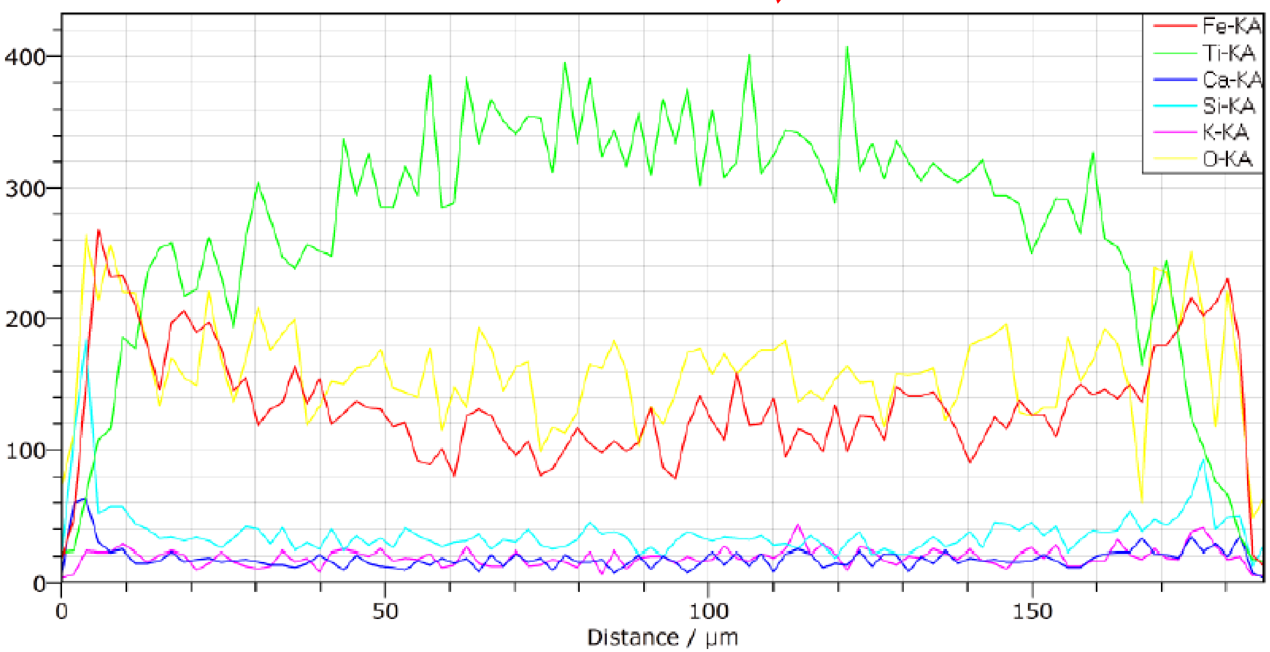


Good appearance
No agglomeration

Day 3 CLG_FR

Fe Ti Ca Si K O

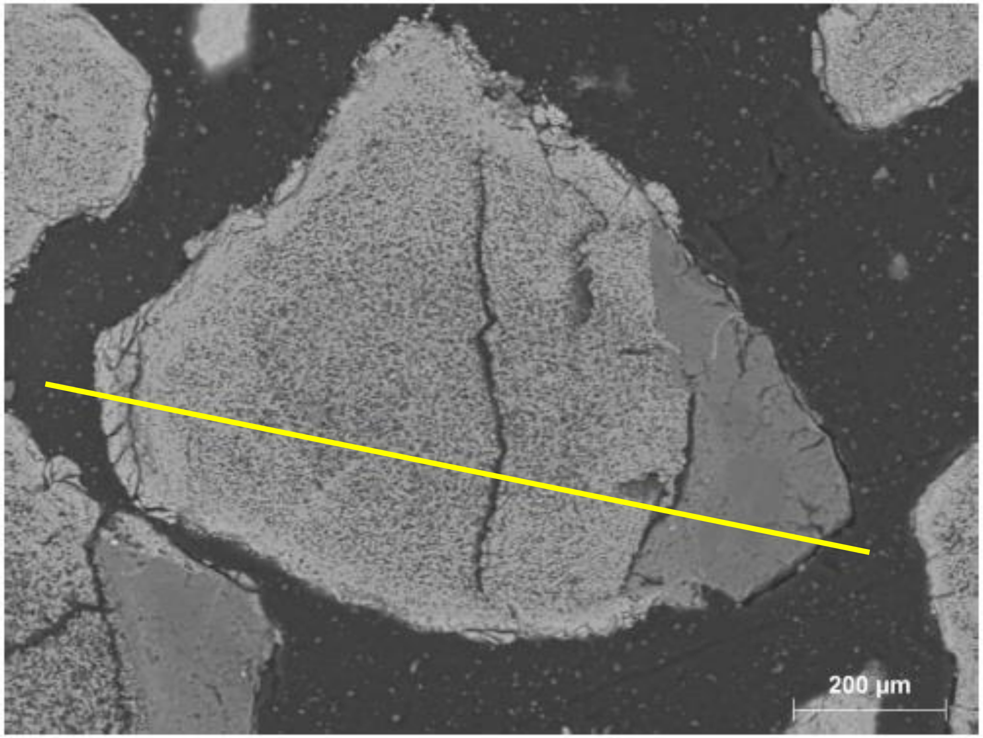




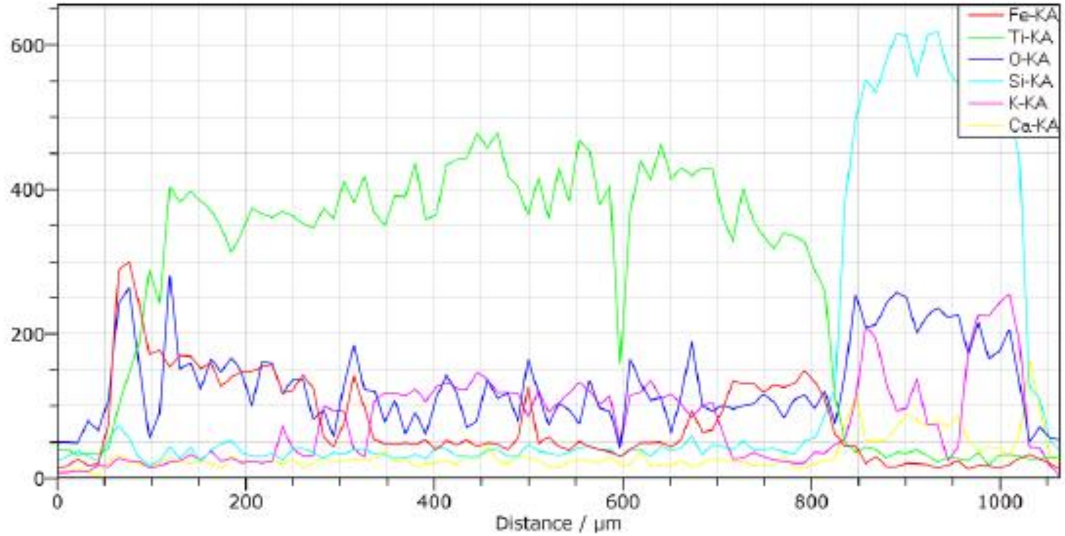
Fe migration towards the external surface of the particles (Fe oxide)

EDX

Day 6 CLG_AR



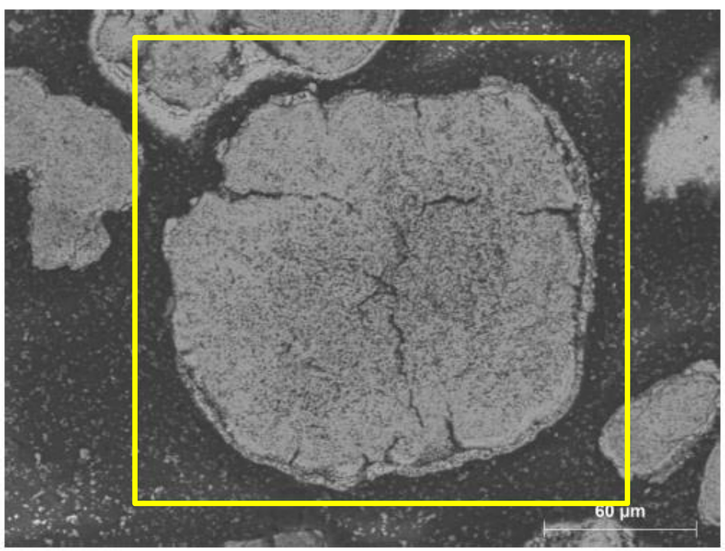
K goes to Si-enriched locations



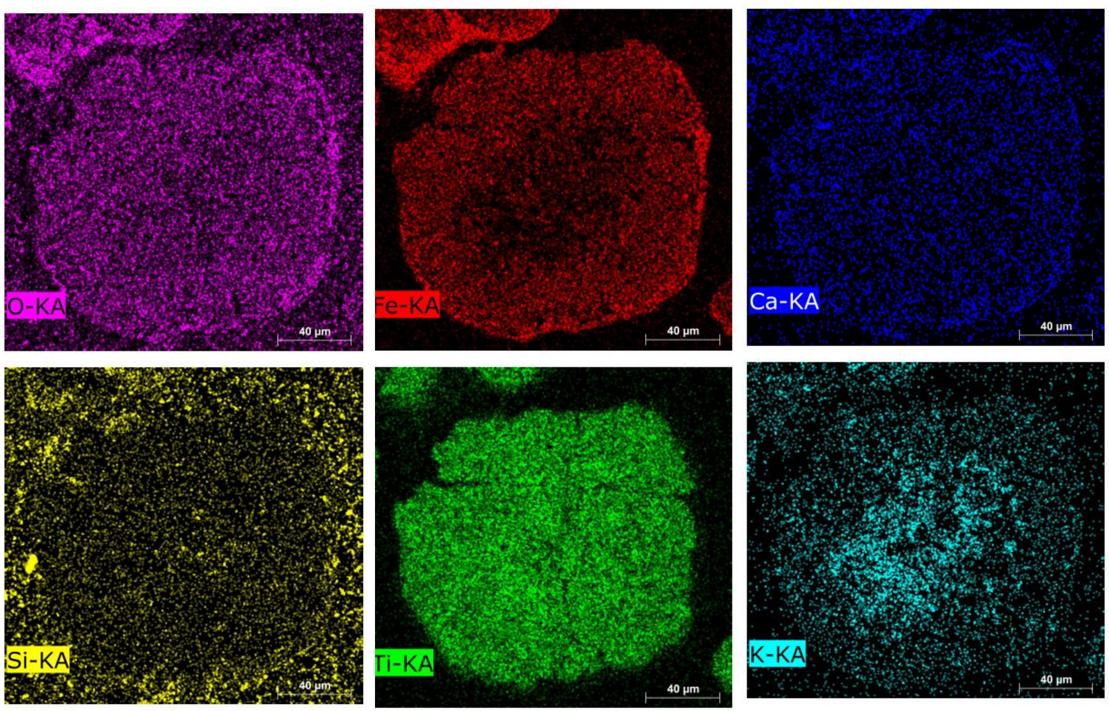
Fe Ti Ca Si K O

Looking for K, Ca and Si

- Some migration of Fe occurs towards the external surface of particle in form of Fe oxide (no Titania).
- K penetrate inside the particles when cracks are present.
- Si and Ca are preferentely deposited in the external layer of the particle.



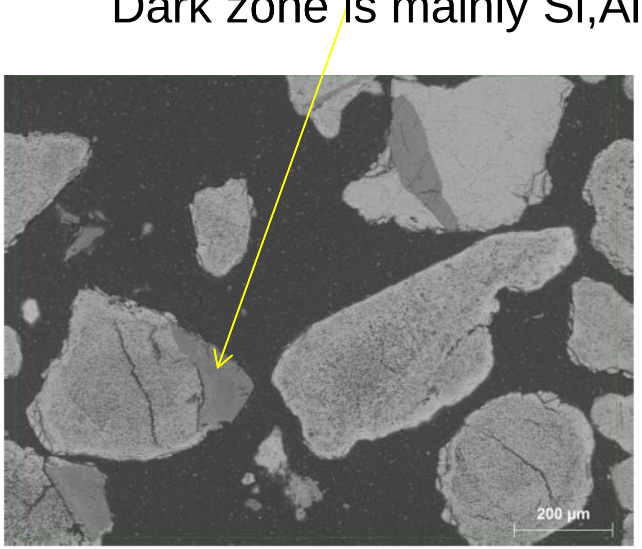
Mapping IlmFRD4-2-x450



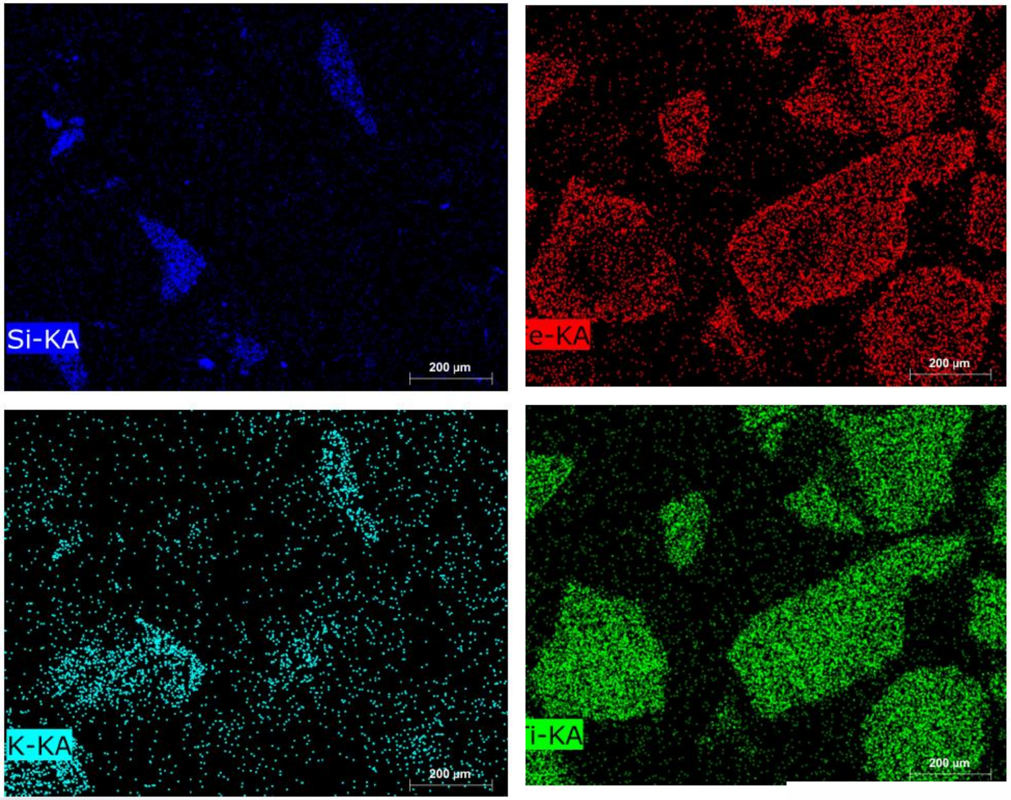
Day 6 CLG-AR

- Fe migration outwards
- K is enriched in zones where Si is present (even if it is inside the particles).

Dark zone is mainly Si,Al-Mg



Mapping IlmARD6-6-x230

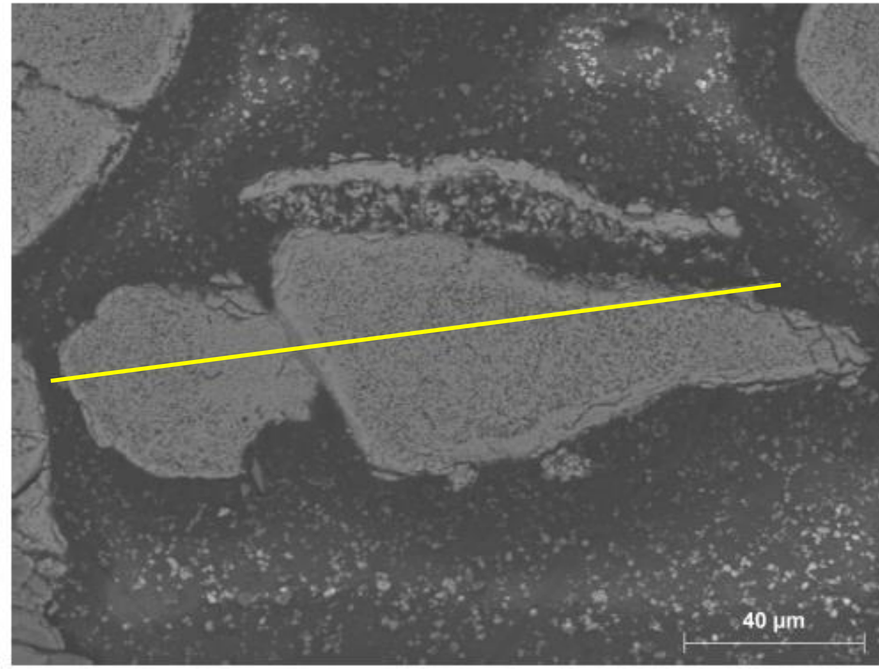


Looking for agglomeration, looking for K

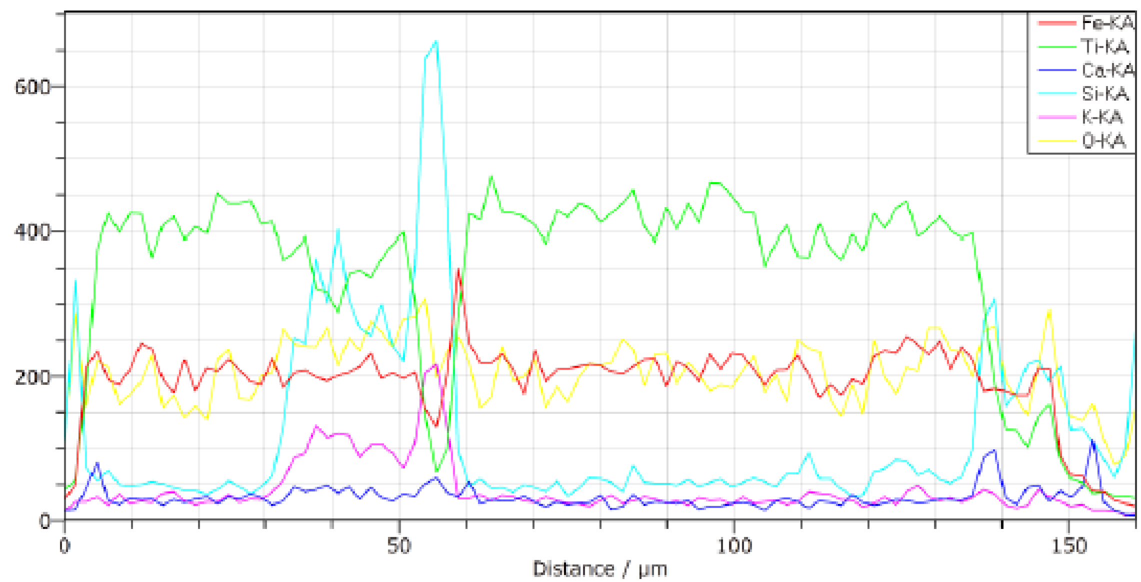
- Particles after 37 h under CLG operation behaved well and no operational problems were observed.

- SEM-EDX studies showed separate particles.
-
- **No agglomeration** was produced.

- In the whole study, only 1 small agglomeration case was observed in day 4 in a particle.



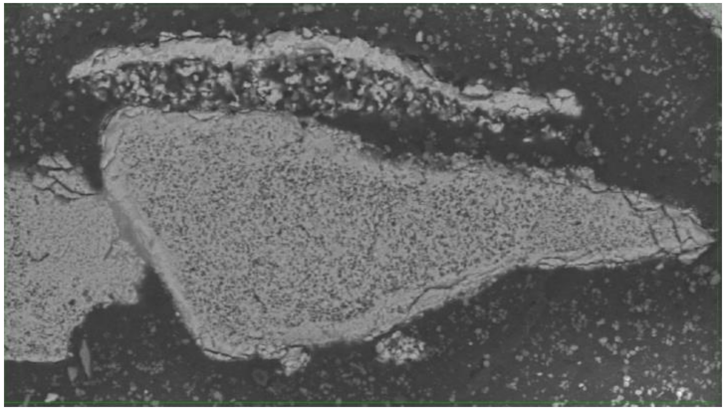
Fe Ti Ca Si K O

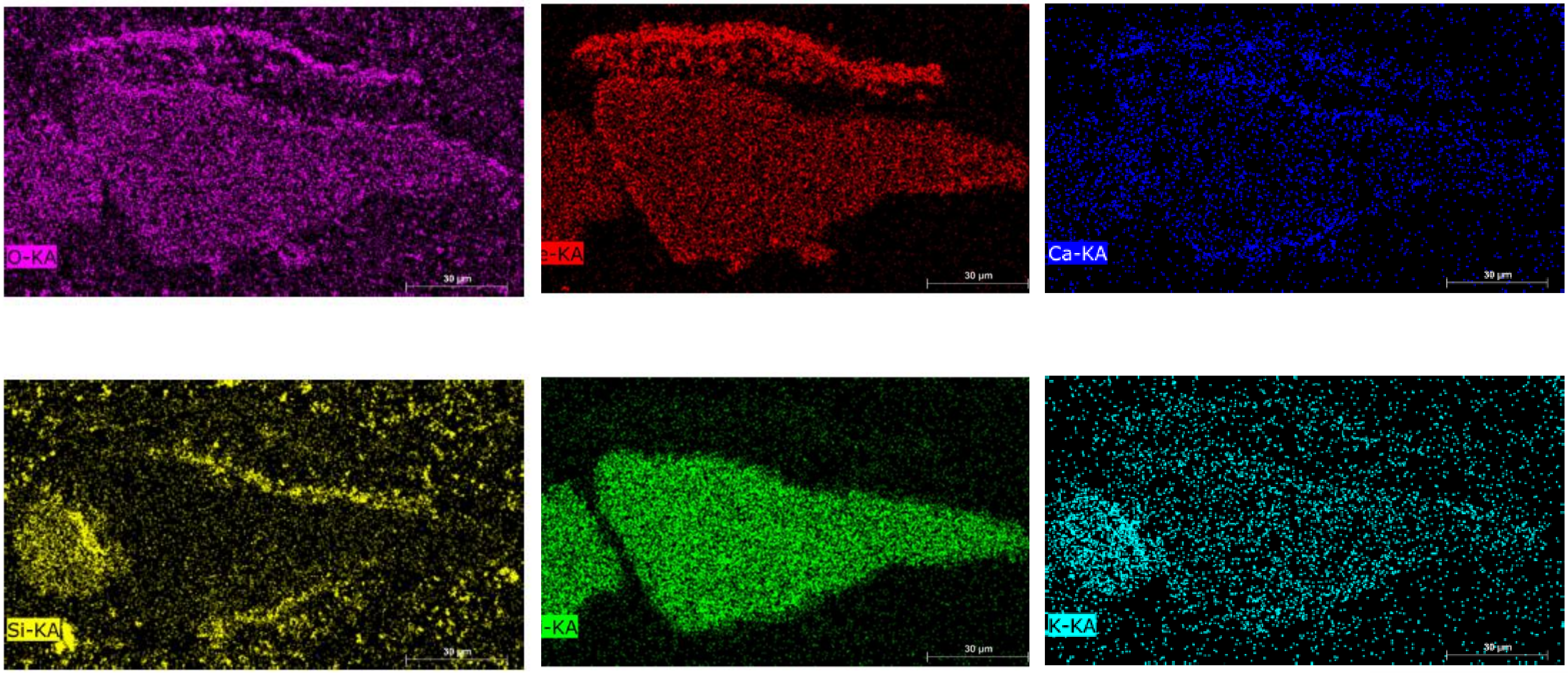


Linescan IlmFRD4-4-x650
Mapping IlmFRD4-3-x800

Looking for agglomeration, looking for K

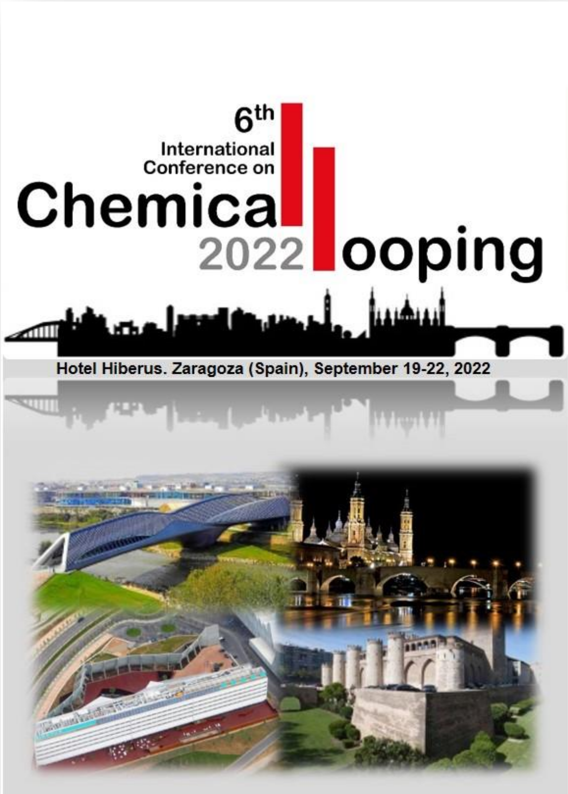
- The shell detached is Fe-O (no Ti)
- K concentrates preferably in Si sites
- Ca and Si seems to be concentrated in the external surface of the particle





Summary (from 50 kW_{th} unit tests)

- **NO agglomeration** was detected during 37 h continuous CLG operation using wheat straw pellets with Ca additive.
- Some migration of Fe outwards the particle surface.
- Some layers detached from particles, but not so relevant as expected.
- Ca, Si an K present in biomass is partially deposited in the oxygen carrier.
- Ca and Si are deposited preferably in the external surface of particles.
- K appeared preferably in Si locations already present on ilmenite.
- K also appeared in internal zones of ilmenite



http://chemical-looping2020.com/

~~Zaragoza (Spain), September 21-24~~

Set the new dates

Zaragoza (Spain), **September 19-22, 2022**

Topics of interest:

- Chemical looping combustion
- Chemical looping gasification/reforming
- Chemical looping oxygen carriers
- Chemical looping reactor design and operation
- Novel chemical looping processes
- Carbonate looping technology
- Modeling of chemical looping process
- Pilot plants and scale-up

We are looking forward seeing you in Zaragoza in 2022

Prof. Juan Adánez
Chairman of the Conference

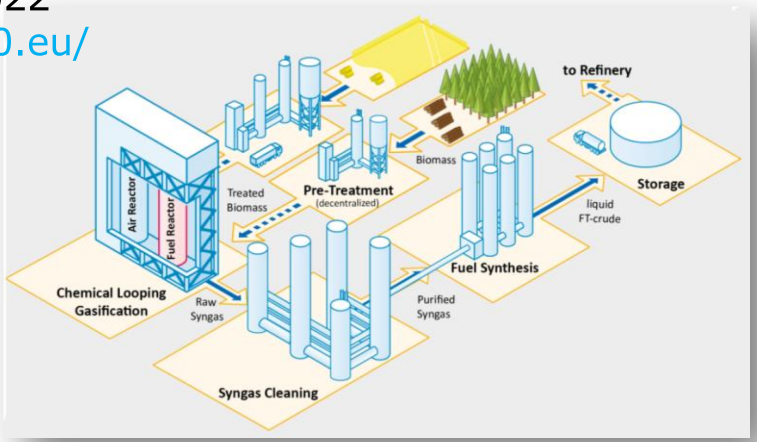
CSIC funding in BCLG

H2020-No. 817841

Chemical Looping Gasification for Sustainable Production of Biofuels

Nov 2018 – Nov 2022

https://clara-h2020.eu/



ENE2017-89473-R

Gasificación de biomasa mediante tecnologías de *Chemical Looping* para produccion de gas de síntesis/H_2 con captura de CO_2

Jan 2018 – Sep 2021

Combustion and Gasification Group

Instituto de Carboquímica (ICB) Zaragoza

Consejo Superior de Investigaciones Científicas (CSIC)

www.icb.csic.es

Research on
Chemical Looping
since 2000

2015 2016 2017 2018

Many Thanks. Questions?