Oxygen carrier selection for chemical looping gasification of biomass based on the results of continuously operated units in the kW-range

WP 3: "Chemical-Looping Gasification"

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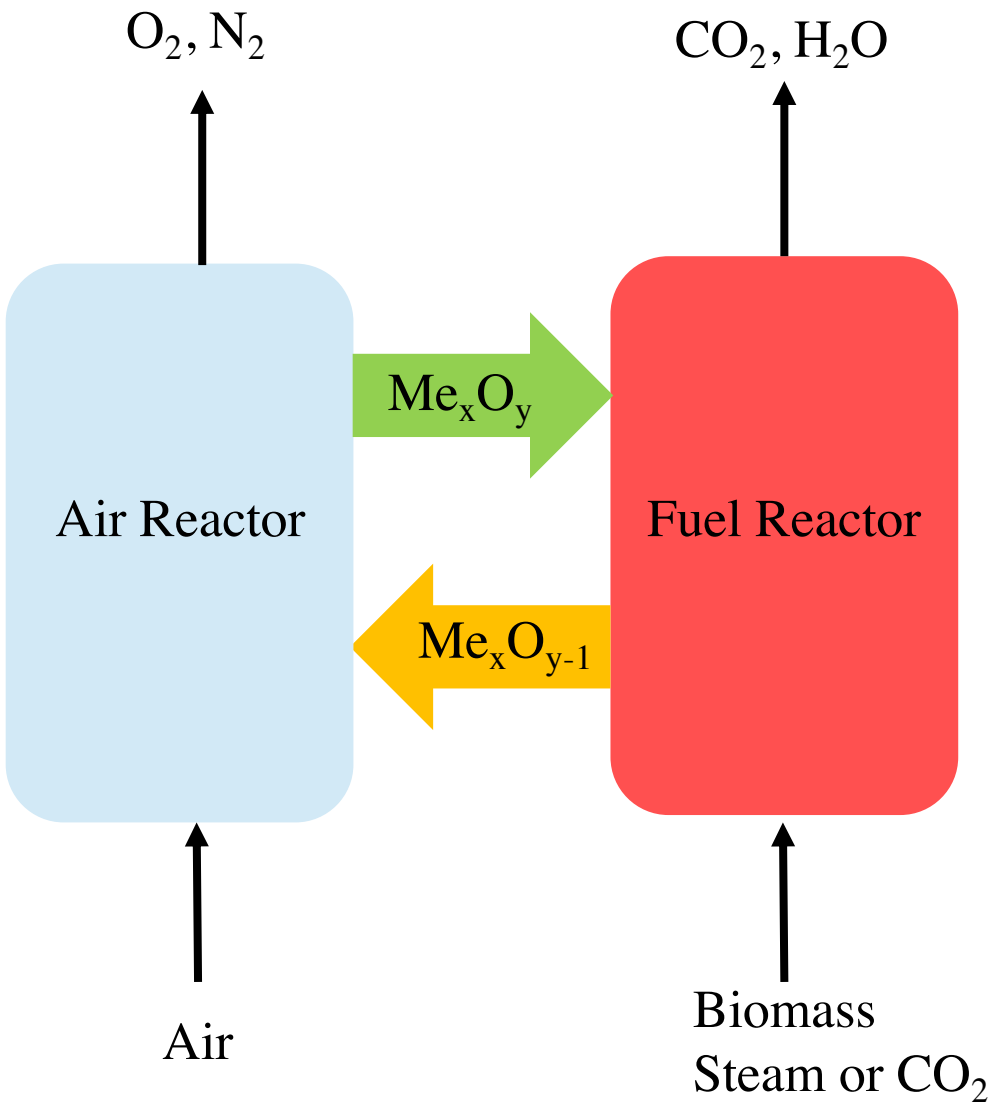
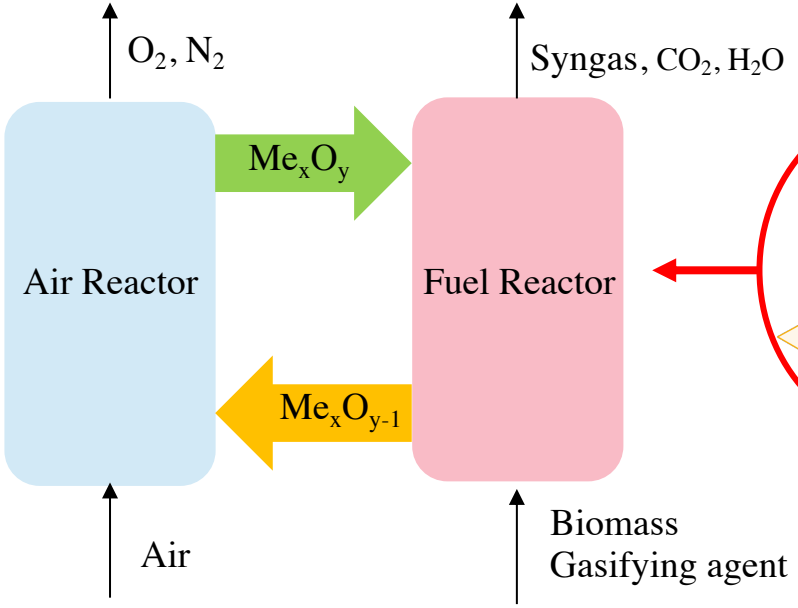
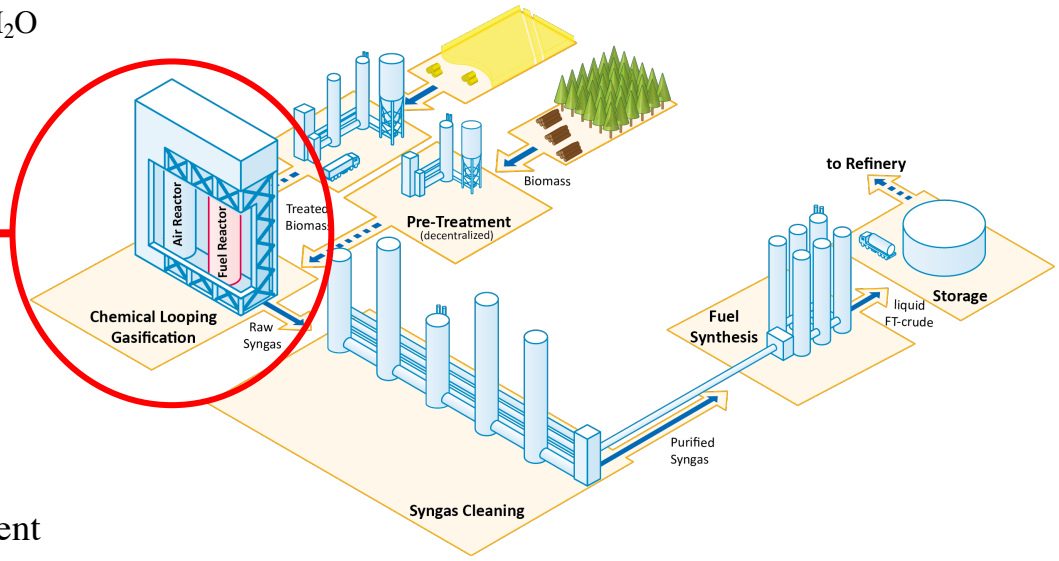
CLARA workshop- April 2021

Chemical looping combustion (CLC)



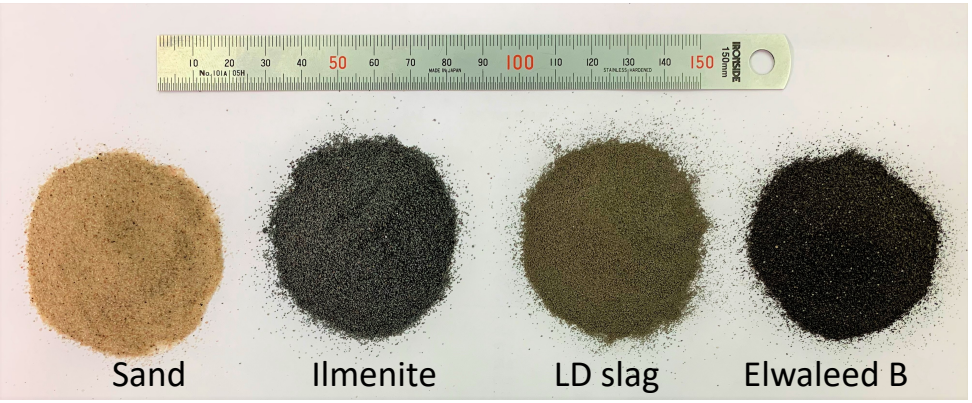
Chemical looping gasification (CLG)





Oxygen carriers:

1. Availability at multi-ton scale
2. Pretreatment of raw materials before using in CLG
3. Capability to convert biomass to gases products
4. Propensities to convert methane
5. Selectivity towards CO and H_2
6. Syngas yield
7. Ability for reducing tar formation
8. Attrition behavior and lifetime
9. Cost



Objectives

- The objective of WP3 is to **establish the viability of the CLG process**.

Specific aims:

- Determine the **functionality of several promising OC** materials at **CLG conditions**.
- Determine the **fate of condensable tar species** using selected OCs.
- Determine **kinetics of char conversion** and **gas reactivity** with selected OCs.
- Develop **models of the two largest CLG reactors** to be used for scale-up to industrial plants.

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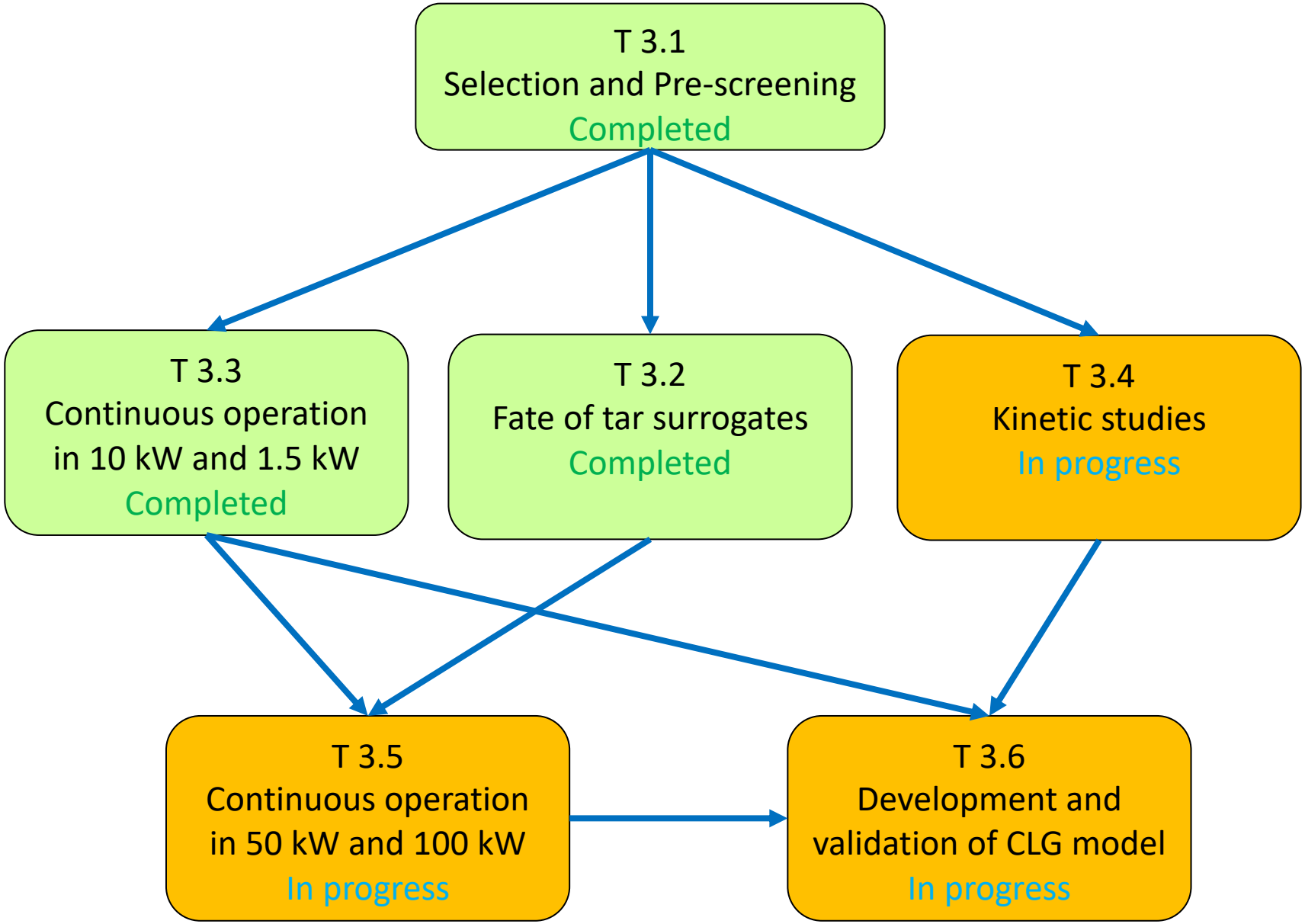
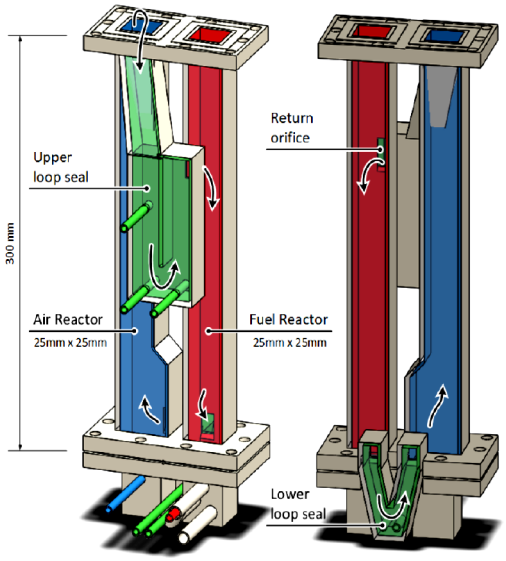
Tasks


T 3.1
Selection and Pre-screening
Completed
T 3.3
Continuous operation
in 10 kW and 1.5 kW
Completed
T 3.2
Fate of tar surrogates
Completed
T 3.4
Kinetic studies
In progress
T 3.5
Continuous operation
in 50 kW and 100 kW
In progress
T 3.6
Development and
validation of CLG model
In progress

Task 3.1
Investigation of potential OC for Chemical Looping Gasification



Preselection of oxygen carriers

- Materials that can be sourced at multi-ton scale
- TGA, batch reactors and 300 W continuous unit
- Behavior with volatiles and syngas combustion

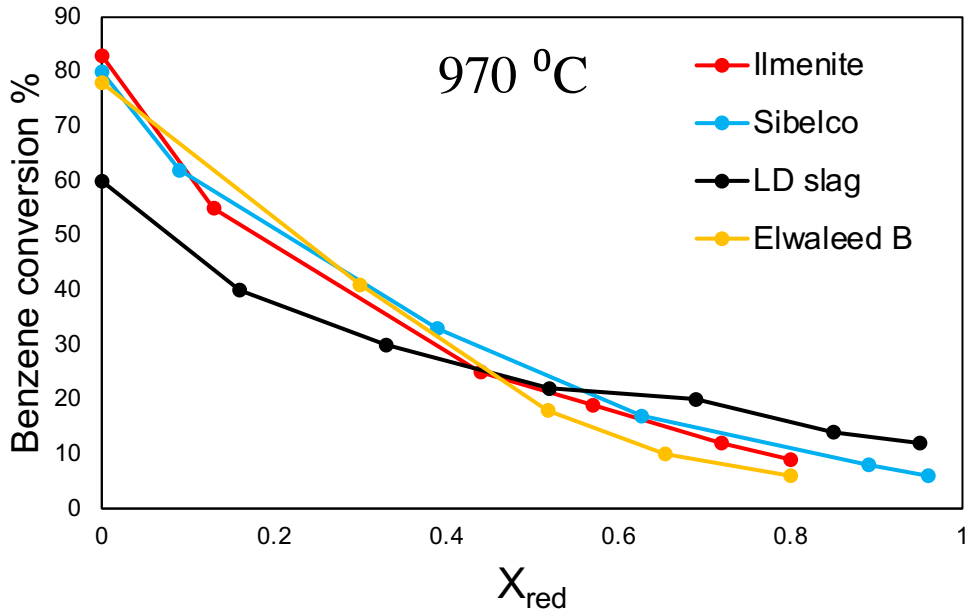
Elemental Composition (wt%)	Moanda-Gabon	Wessels (South Africa)	Sibelco	Egyptian Ore	Tierga	Ilmenite	LD slag
	Mn ore	Mn ore	Mn ore	Mn-Fe ore	Fe ore	Fe-Ti ore	Fe waste
Mn	46.7	39.8	49.9	32.3	0.05	0.2	2.2
Fe	5.1	14.6	5.2	21.6	54.9	33.1	13.7
Si	4.2	3.3	3.4	4.7	3.8	0.9	4.8
Al	3.8	0.2	4.2	1.2	2.1	0.3	0.5
Ca	-	-	1.9	1.7	-	0.2	27.3
			Oxygen Carrier performance				
R_{OC} (%)	5.0	4.7	4.7	4.1	2.5	5.0	0.46
RI_{CH4}/RI_{H2}	0.14	0.07	0.22	0.30	0.27	0.63	0.35
AJI index (%)	16.8	5.5	1.6	8.8	6.3	2.4	4.6

Task 3.2
Investigation of fate of tar surrogates with OC materials

Conversion of tar species with the selected OCs:

- Partial oxidation through transfer of oxygen from OCs
- Catalytic and thermal cracking/reforming on the surface of OC

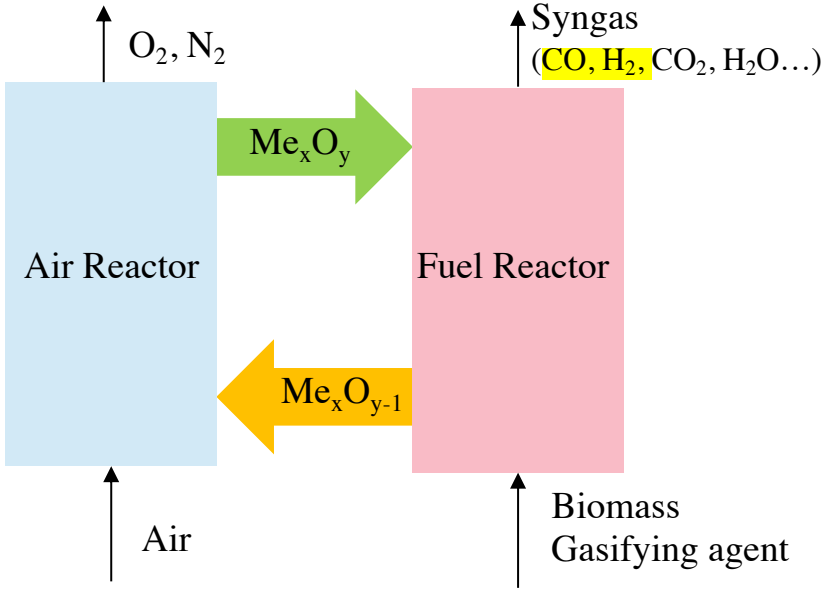
H_2O	CO_2 CO H_2 CH_4 C_2-C_3	Condensable hydrocarbons (Tar)



Task 3.3
Testing of oxygen carriers in continuous operation

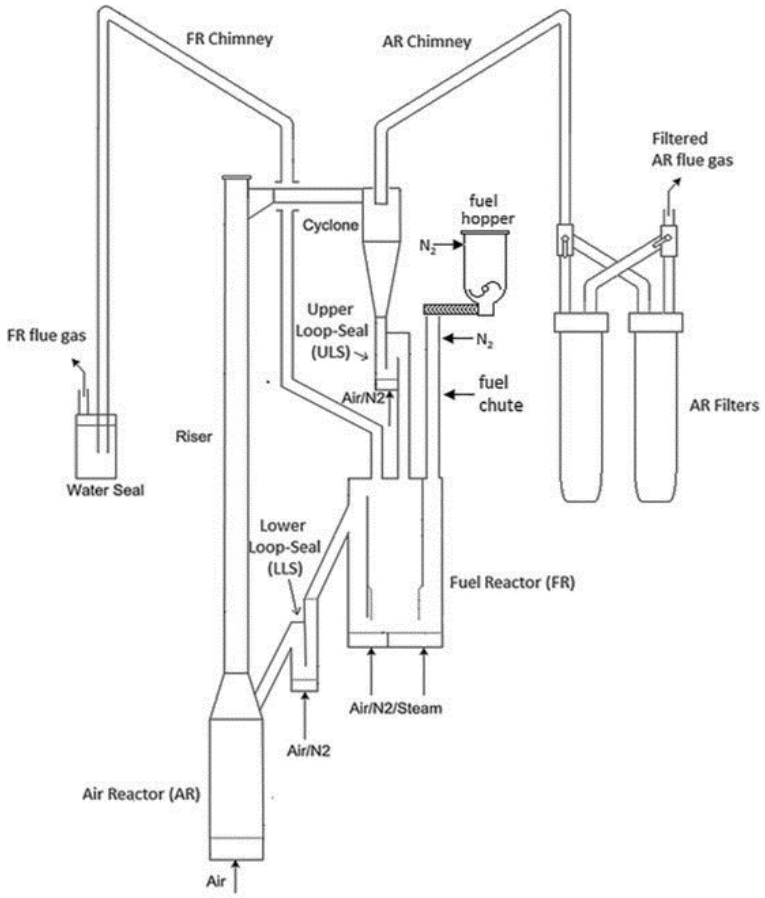
Selected oxygen carriers are investigated in continuous operation using solid biomass fuels in the 1.5 kW_{th} reactor at CSIC and 10 kW_{th} reactor at CTH.

- Decreasing the oxygen provided to FR by controlling the OC circulation rate
- The control of the oxygen transfer rate by using typical CLC oxygen carriers diluted with an inert (i.e. olivine or sand).
- Feeding the amount of oxygen, required in the FR for syngas production, into the AR.



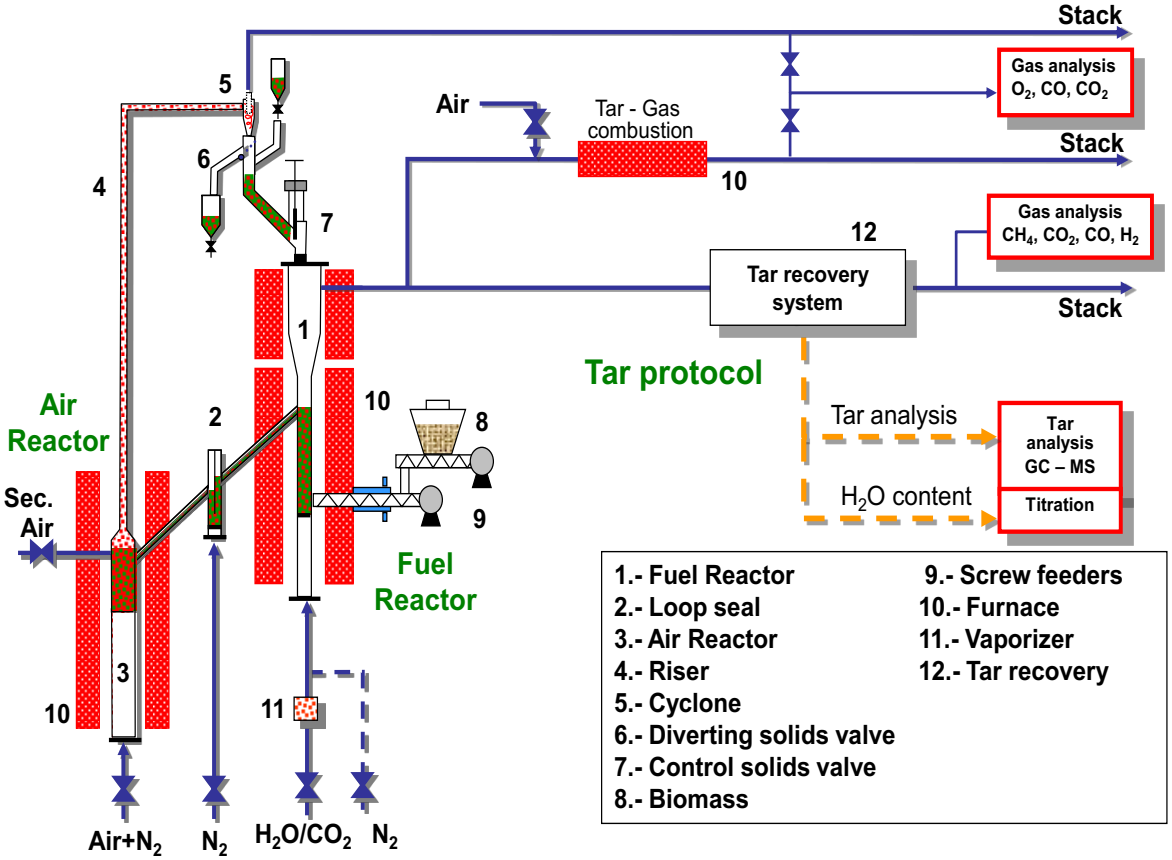
10 kW_{th} unit at CTH

Operation parameter	Unit	Oxygen carrier
Oxygen carriers		Ilmenite, LD slag, Elwaleed B, Silica Sand
Biomass		Pine forest residue, Straw pellets, Black pellets
Temperature	°C	820 - 970
Steamt to biomass ratio	$kg/kg_{drybiomass}$	0.8 - 1.9
Oxygen to fuel ratio (λ)	mol/mol	0.1 - 0.7



1.5 kW_{th} unit at CSIC

Operation parameter	Unit	Oxygen carrier
Oxygen carriers		Ilmenite, LD slag, Tierga, Moanda Mn ore
Biomass		Pine forest residue
Temperature	°C	820 - 940
Steamt to biomass ratio	$kg/kg_{drybiomass}$	0 - 06
Oxygen to fuel ratio (λ)	mol/mol	0.15 - 0.5



Performance evaluation

Biomass conversion

$$X_b = \frac{\text{carbon in gases from FR and AR}}{\text{carbon in biomass}}$$

Syngas yield and H_2/CO ratio

$$Y = \frac{\text{flow of } H_2 + CO \text{ from FR (mol/h)}}{\text{biomass feeding rate (kg/h)}}$$

Carbon conversion efficiency

(carbon capture in CLC)

$$\eta_{CC} = \frac{\text{carbon converted to gas in the FR}}{\text{carbon in biomass}}$$

Cold gas efficiency

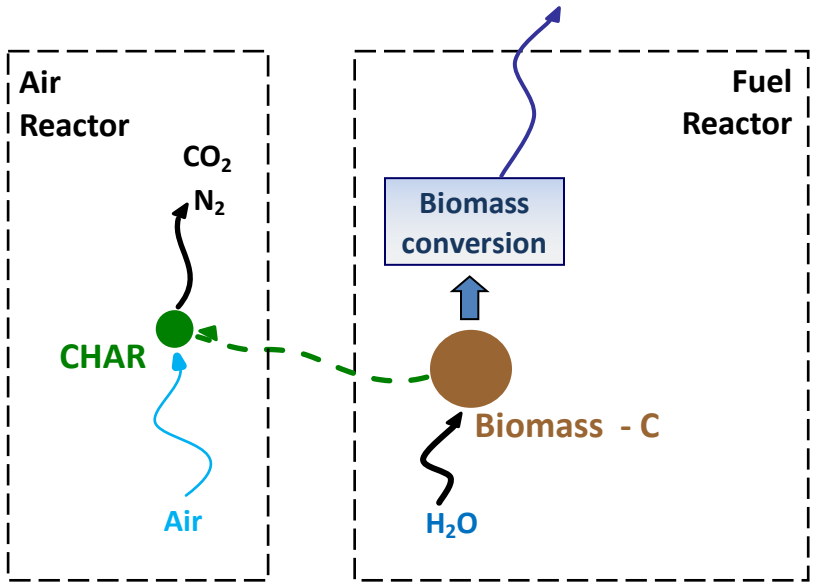
$$\eta_g = \frac{\text{chemical energy in gases FR (kJ/h)}}{\text{energy in biomass (kJ/h)}}$$

Solid Products

- C + ash

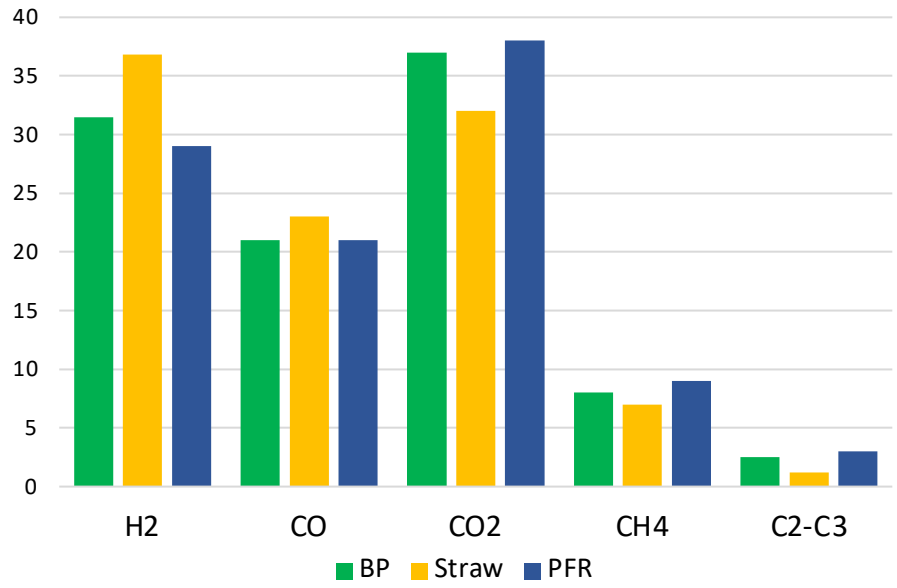
Gaseous Products

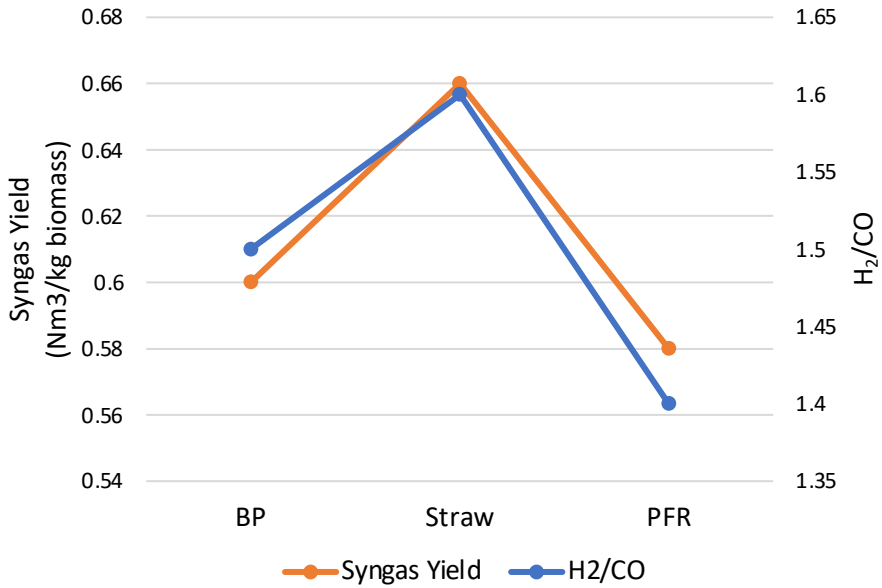
- Syngas: H_2 + CO
- HCs: CH_4, C2s, C3s, etc.
- Tar: higher HCs
- Combustion products: CO_2



CLG with different biomass

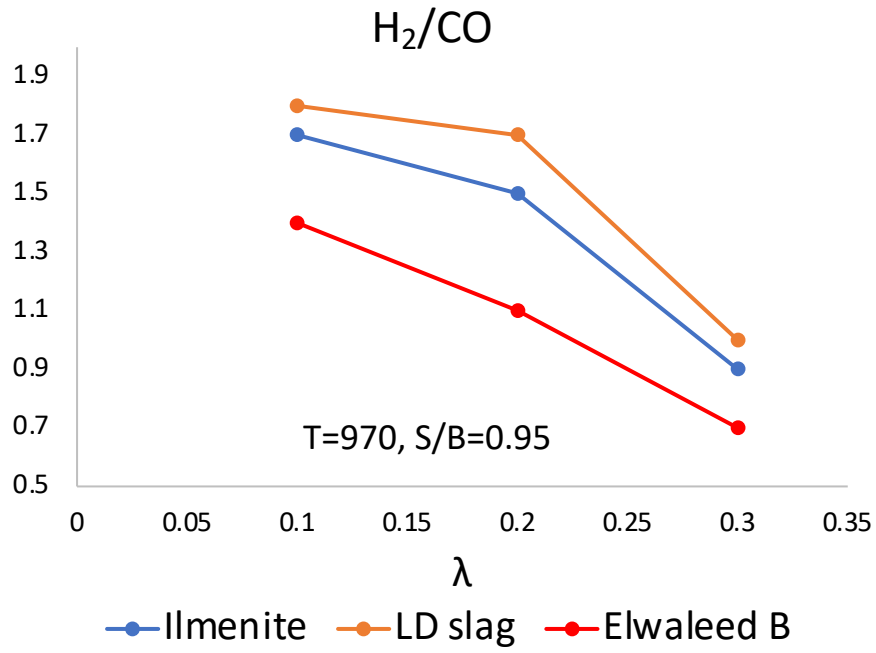
	Straw Pellets (Straw)	Pine forest residue (PFR)	Black wood pellets (BP)
Moisture	8.8	8.0	6.9
Ashes	7.9	0.4	0.3
Volatile matter	75.0	77.8	74.2
Fixed carbon	8.3	13.8	18.7



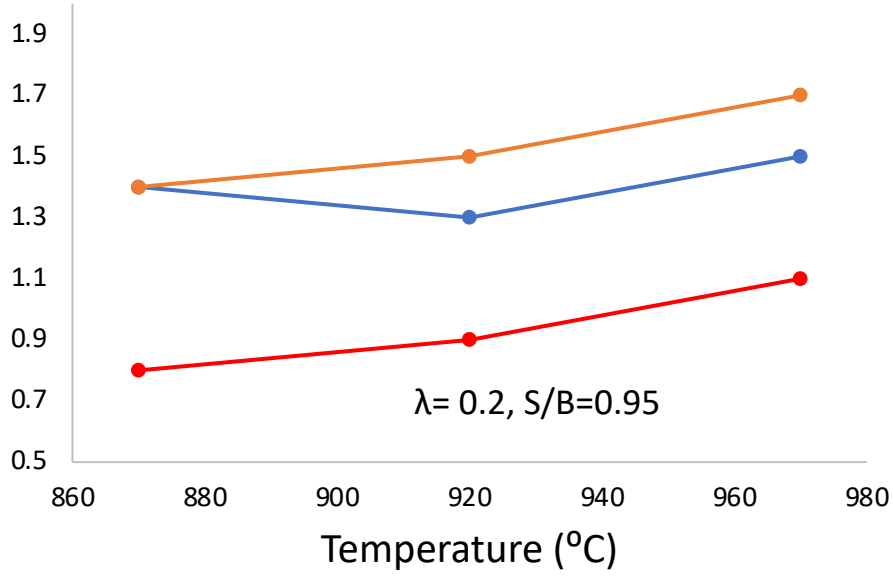


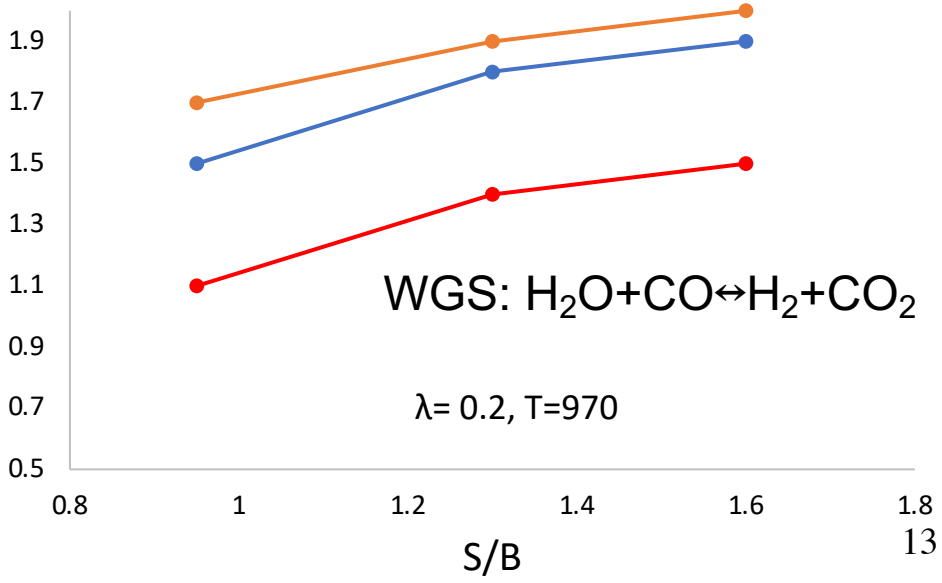
Ilmenite, S/B=0.95, λ= 0.2, T=870

Effects of operating parameters



Fuel: PFR



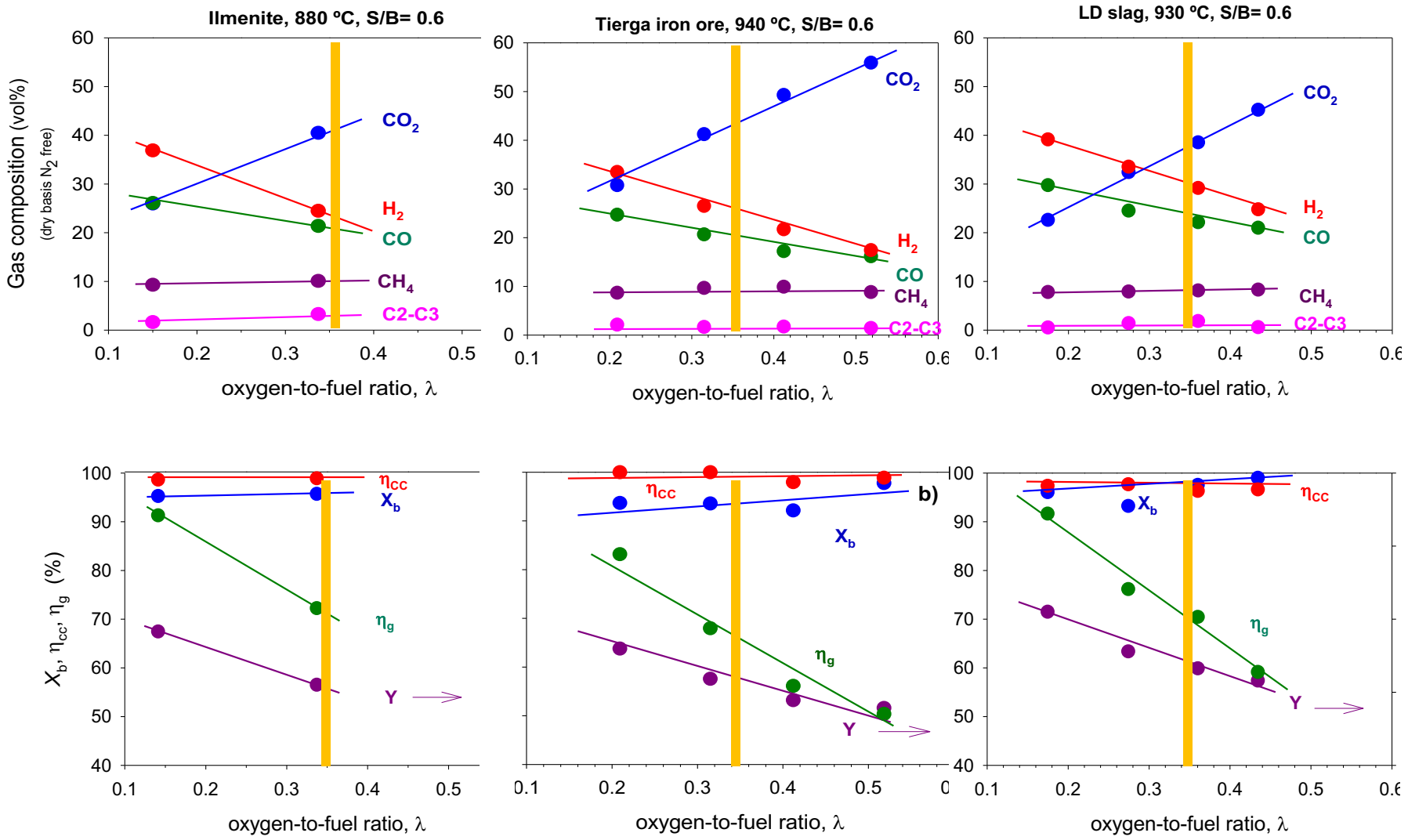


Comparison of OCs' performance

2 Ilmenite

3 Tierga

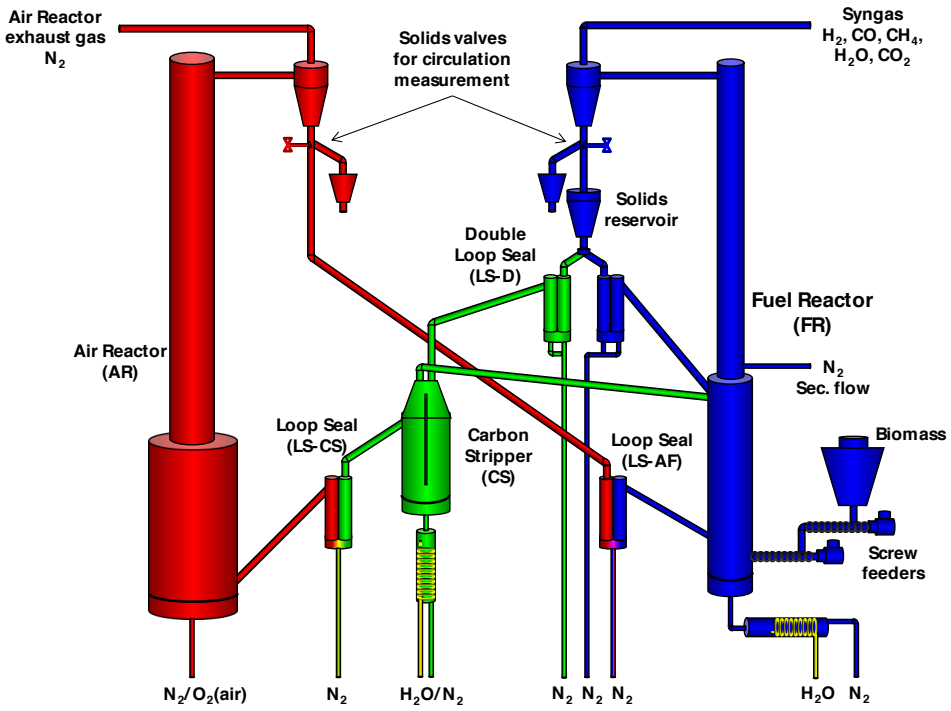
1 LD slag



Ilmenite and LD slag: CSIC and CTH

Gas composition	Unit	Oxygen Carrier			
		CTH S/B=0.95, T=970ºC, λ=0.2, Fuel=PFR		CSIC S/B=0.6, T=950ºC, λ=0.35, Fuel=PFR	
		Ilmenite	LD slag	Ilmenite	LD slag
CO_2	%vol	37	35	41.5	38.1
CO	%vol	22	20	21.1	23.1
H_2	%vol	29	34	23.6	29.5
CH_4	%vol	8	8	10.2	8.1
C_2-C_3	%vol	4	3	3.4	1.2
Biomass conversion, X_b	%	93	95	98.9	97
H_2/CO	-	1.5	1.7	1.1	1.3
Syngas yield, Y	m^3/kg dry biomass	0.65	0.71	0.53	0.70
Tar	g/Nm^3	8-18	3-8	1-2	2-3
Lifetime	hour	850	800	630	275
Cost	USD/Ton	200	-	200	-

Task 3.4. Continuous CLG in 50 kW_{th} unit at CSIC



Operating conditions	
T= 980 ºC	
λ= 0.3	
S/B= 0.7	

Gas composition (vol%)	
CO_2	27.4
CO	23.3
H_2	38.3
CH_4	9.8
C2-C3	1.3
Syngas yield, Y	0.61

- 30 h of continuous CLG operation with ilmenite and Wheat Straw pellets with additives
- Investigated the effect of the main operating variables (λ, T, S/B)
- Product gas also contains CH_4 concentrations around 8 vol %.
- No agglomeration was found during continuous CLG operation

Outcomes

- Six iron and manganese ores and one by-product from the steel industry had been preselected as oxygen carriers for CLG
- A total number of 300 hours experiments has been done in a prescreening step
- More than 600 hours of continuous CLG operation have been carried out at steady state using five oxygen carriers
- The tests demonstrated that it is possible to obtain a high purity syngas, with low tar production with the ores and wastes tested.
- High hydrocarbons contents were found, especially CH_4, where values up to 10% are usual.
- The highest syngas yield was obtained with LD slag and ilmenite.
- Tar concentration was lower than conventional steam gasification.
- Lifetime of oxygen carriers is lower than that found in combustion conditions for the same oxygen carrier. Best extrapolated lifetime was found for ilmenite.
- LD slag and ilmenite are considered as the best performance oxygen carriers for CLG

Thanks for your attention