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Comparison of a full range of oxygen carrier materials for Chemical Looping Coal Combustion

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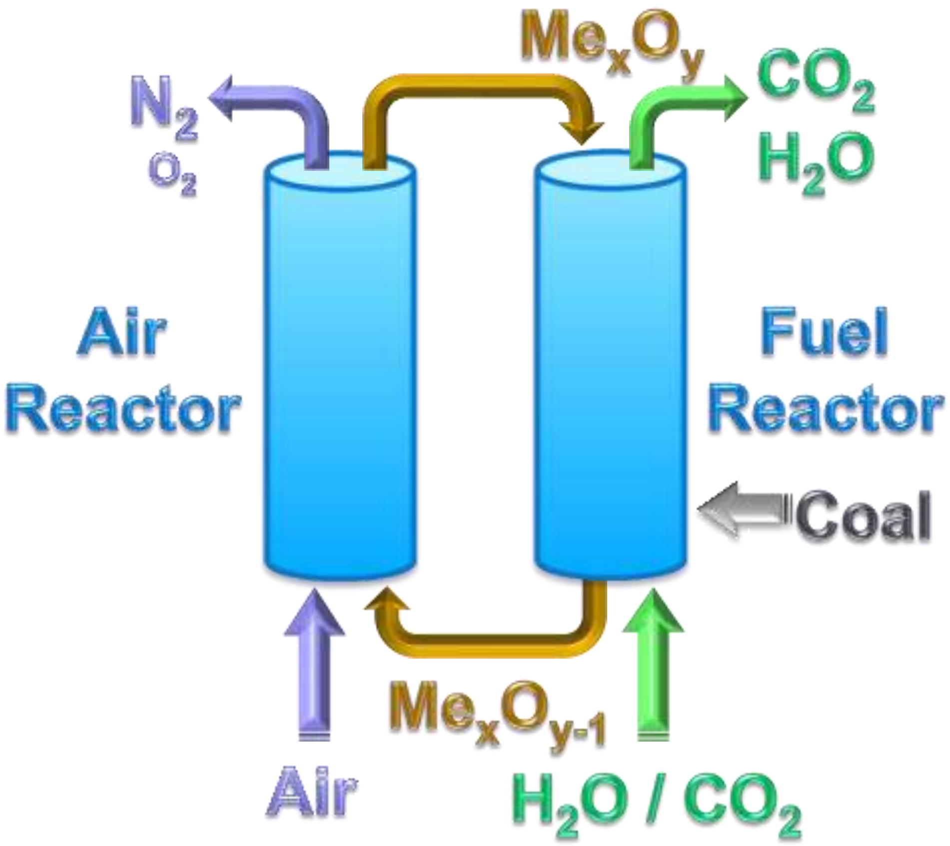
CLC Process



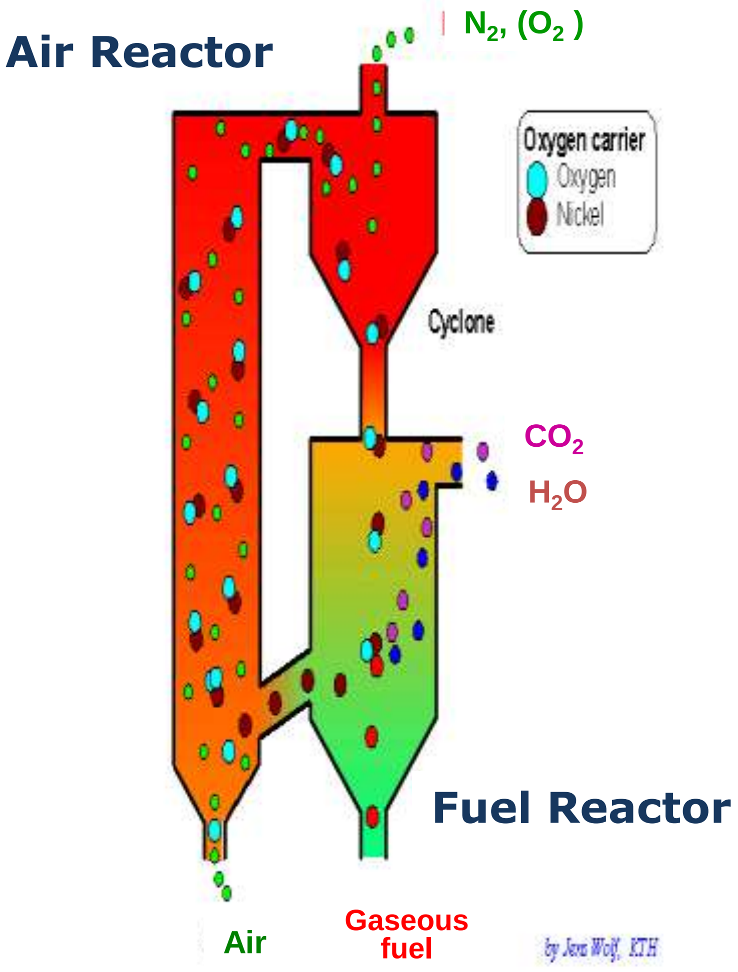
CO_2 capture is inherent to the process

Same energy as conventional combustion

Less energy penalty for carbon separation

Reduction (FR)	**Fuel + Me_xO_y**	$\longrightarrow$	**Me_xO_{y-1} + CO_2 + H_2O**	**ΔH_r**
Oxidation (AR)	**O_2 + Me_xO_{y-1}**	$\longrightarrow$	**Me_xO_y**	**ΔH_o**
Total	**Fuel + O_2**	$\longrightarrow$	**CO_2 + H_2O**	**$\Delta H_c = \Delta H_r + \Delta H_o$**

CLC Configurations



Interconnected reactors

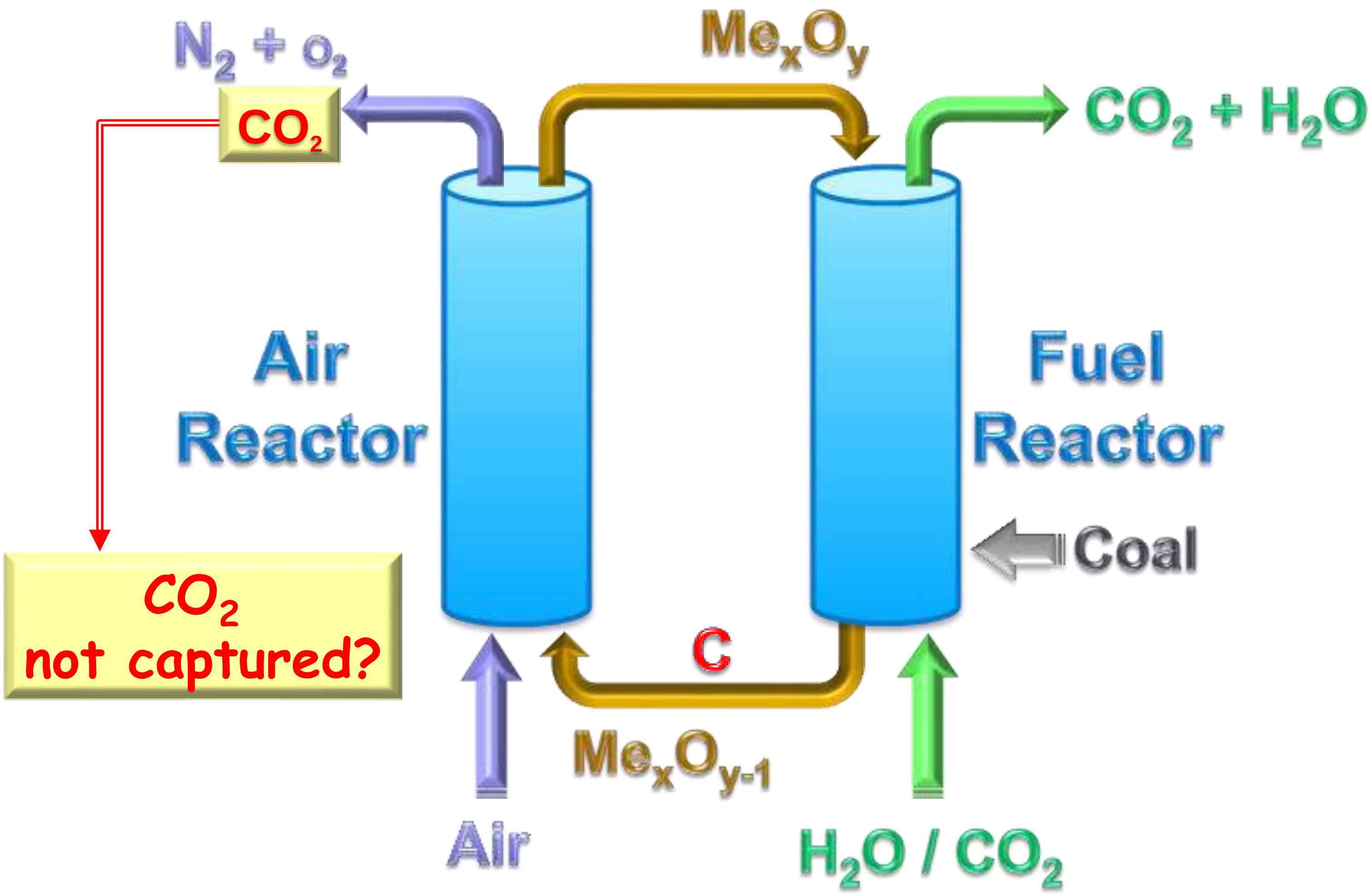
- ✓ fluidized beds
  scale-up is easier
- ✓ moving/fluidized
- ✓ fixed bed
  developed to operate under pressure

Interconnected fluidized beds

- ✓ Different configurations are possible
- ✓ High and stable solid circulation
- ✓ Stable temperature
- ✓ Commercial technology (CFB boilers)
- ✓ Some difficulties for pressure operation

CLC Main Challenges

Unburnt carbon



$N_2 + O_2$

CO_2

Me_xO_y

$CO_2 + H_2O$

Air Reactor

Fuel Reactor

Coal

CO_2 not captured?

C

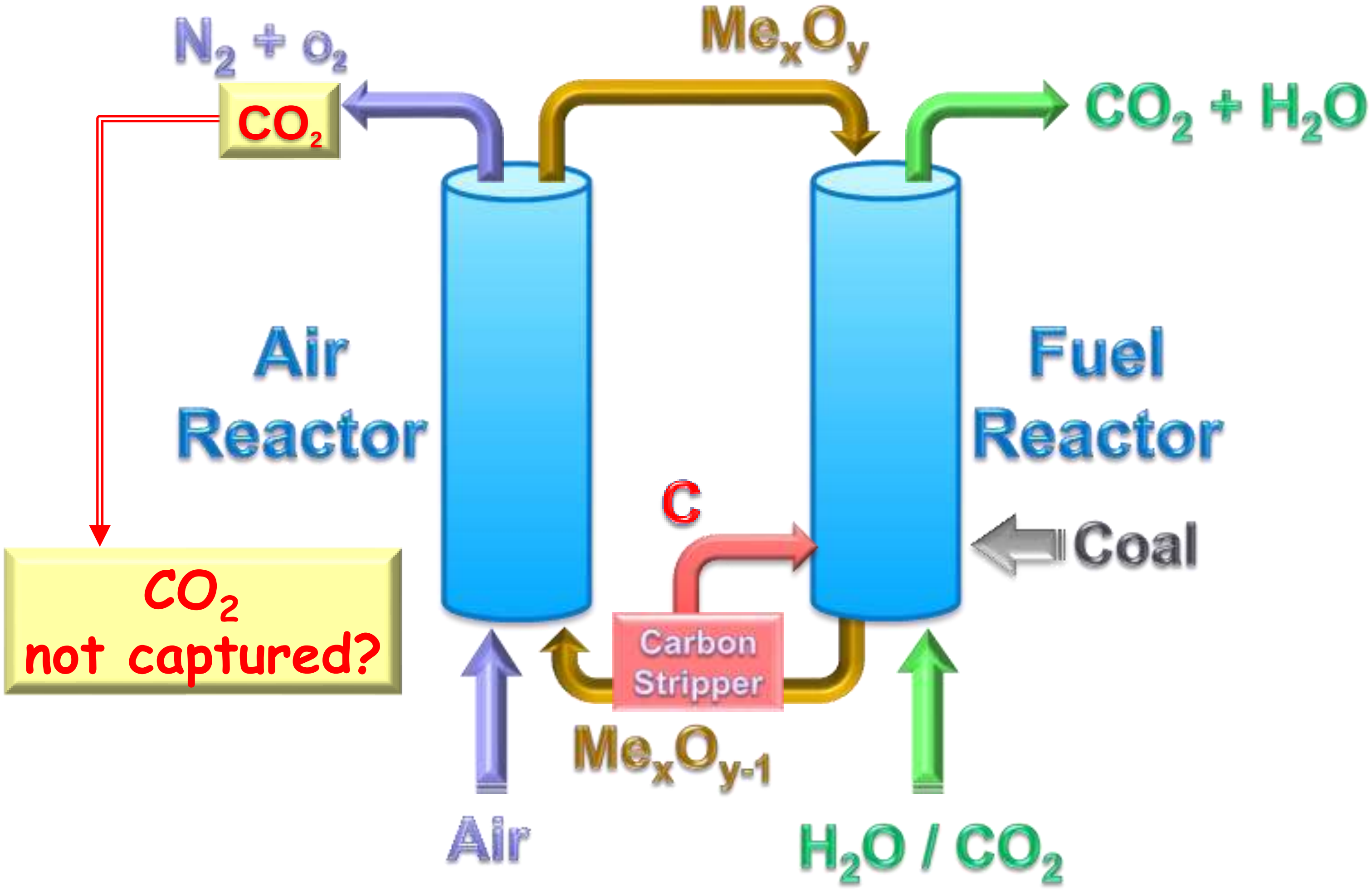
Me_xO_{y-1}

Air

H_2O / CO_2

CLC Main Challenges

Unburnt carbon



$N_2 + O_2$

CO_2

Me_xO_y

$CO_2 + H_2O$

Air Reactor

Fuel Reactor

C

Coal

CO_2
not captured?

Carbon Stripper

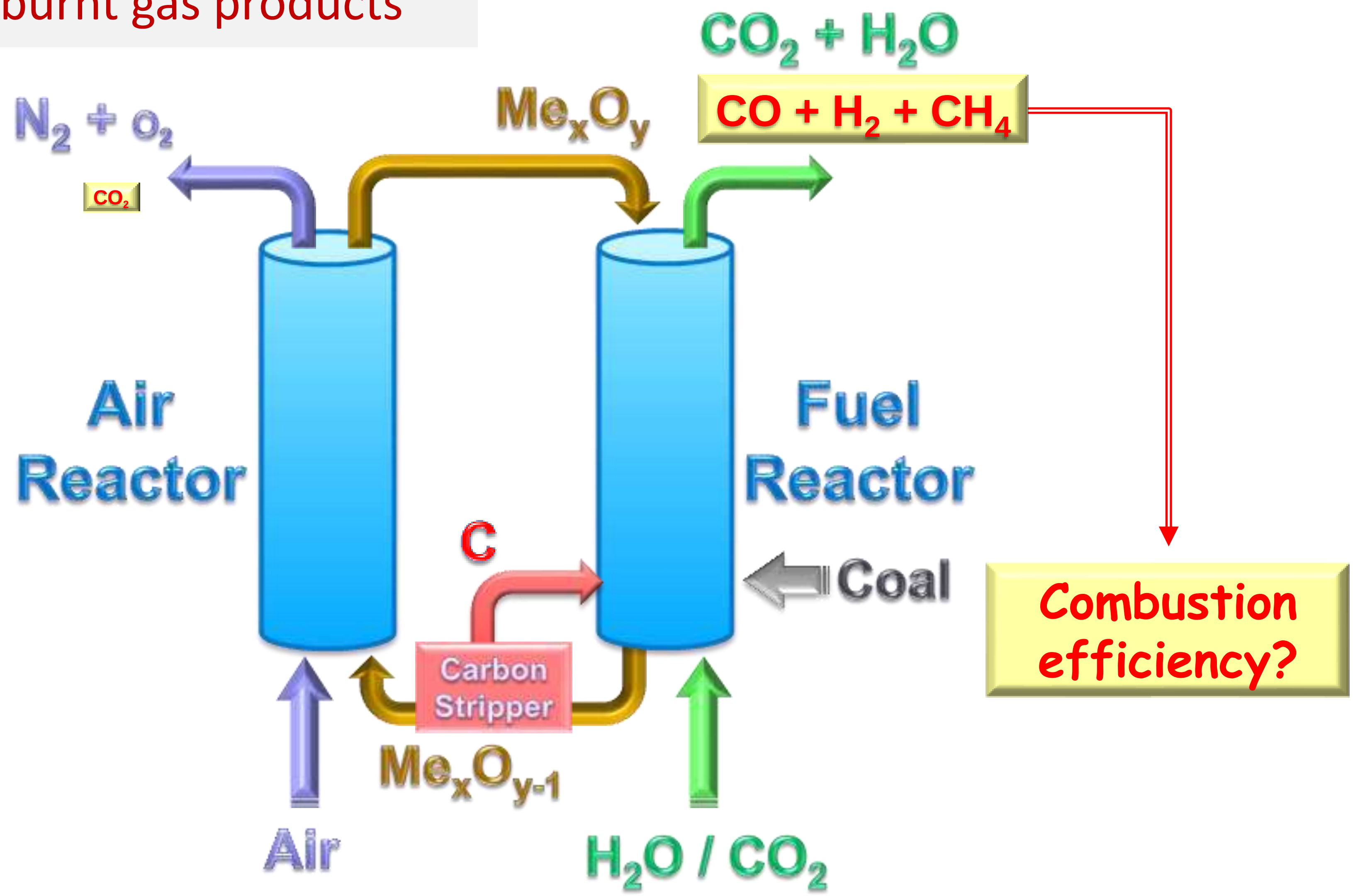
Me_xO_{y-1}

Air

H_2O / CO_2

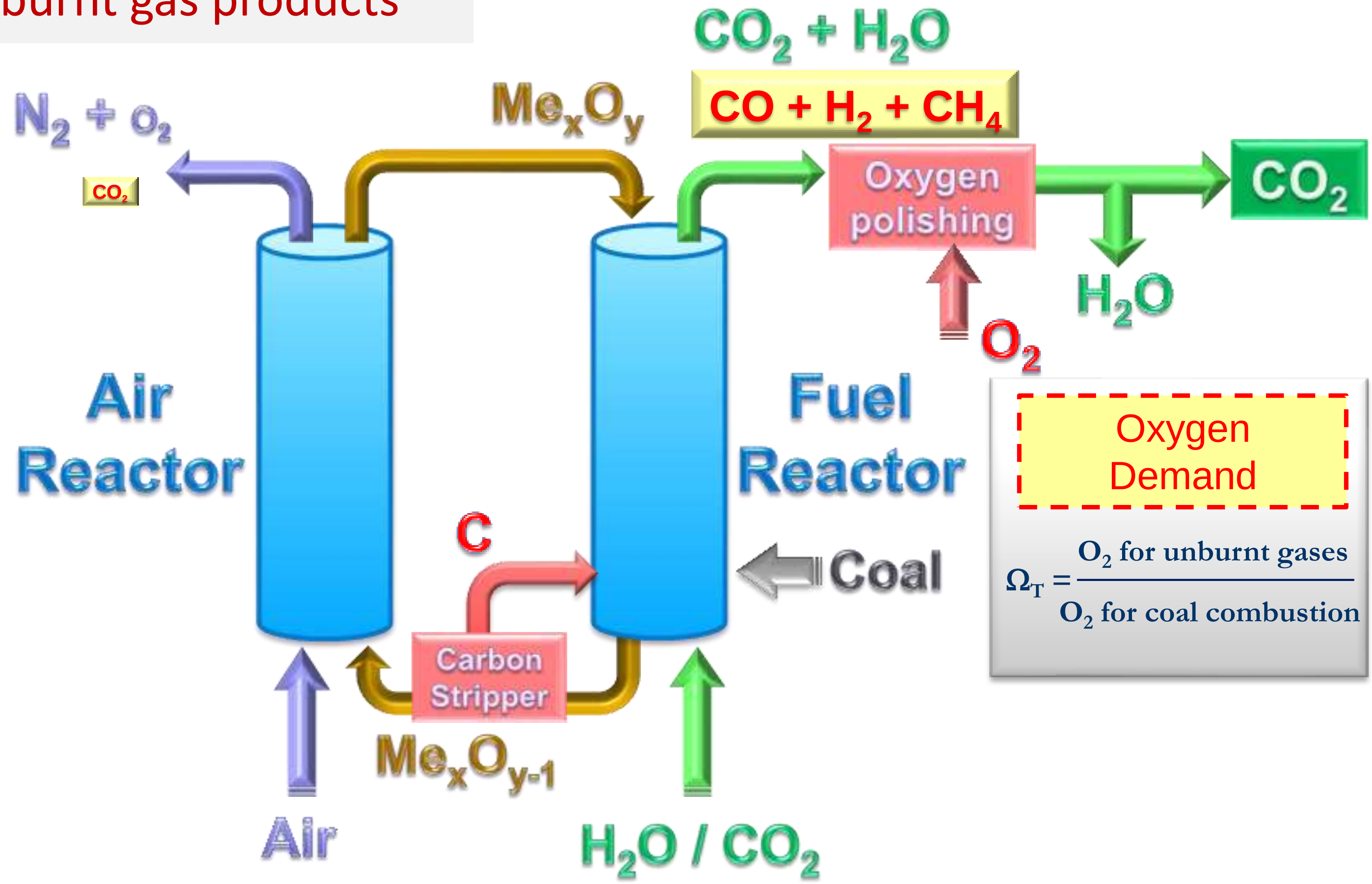
CLC Main Challenges

Unburnt gas products



CLC Main Challenges

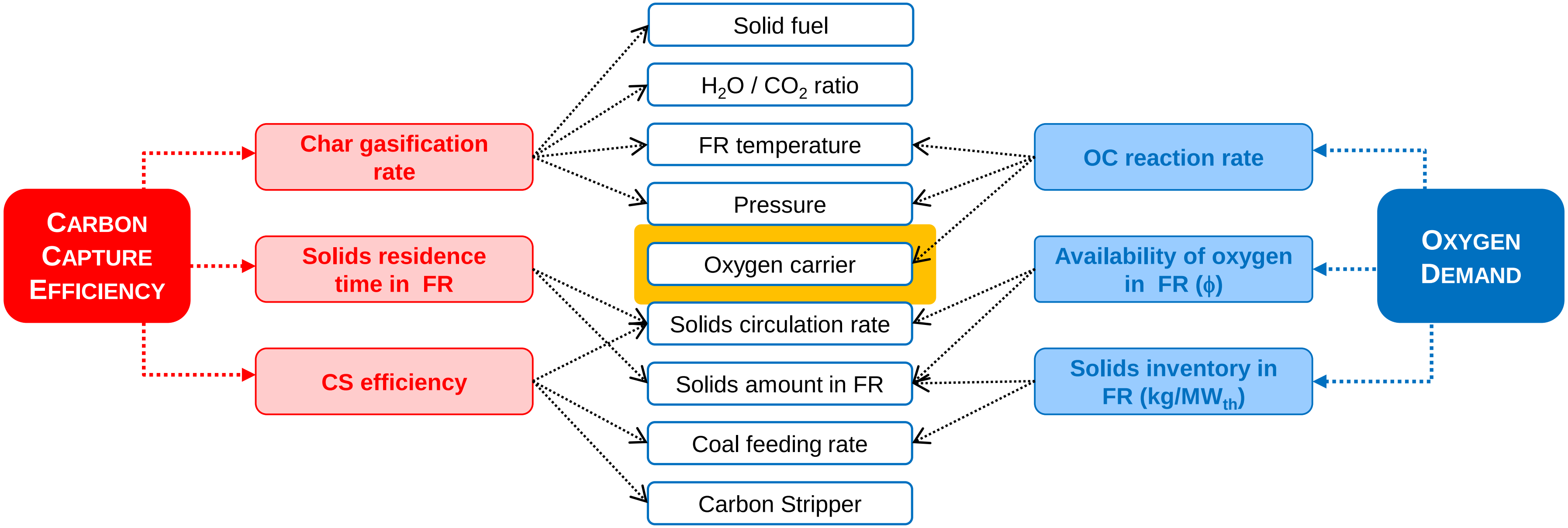
Unburnt gas products



Oxygen Demand

$$\Omega_T = \frac{O_2 \text{ for unburnt gases}}{O_2 \text{ for coal combustion}}$$

CLC Main Factors



Oxygen carrier material is a key point in CLC development

Oxygen carrier properties can affect CLC performance on several areas, such as oxygen demand, carbon capture efficiency, operating costs, enviromental issues…

CLC Oxygen Carriers

- ✓ It is the cornerstone of the process and transport oxygen and heat between reactors.
- ✓ Different redox pairs have been used for CLC

NiO/Ni, CuO/Cu, Fe_2O_3/Fe_3O_4, Mn_3O_4/MnO,

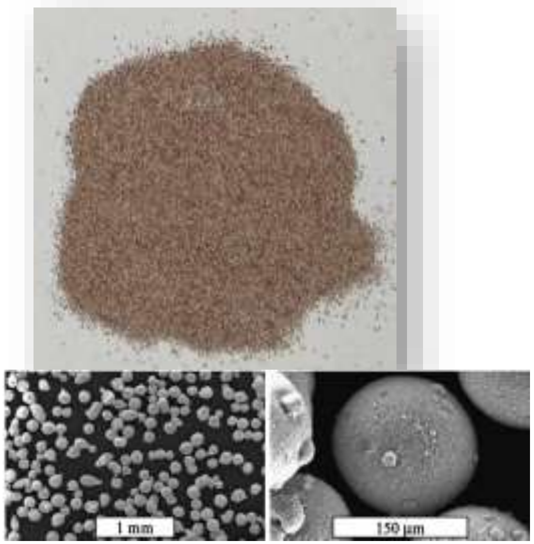
$CaSO_4/CaS$, mixed oxides

Selection criteria

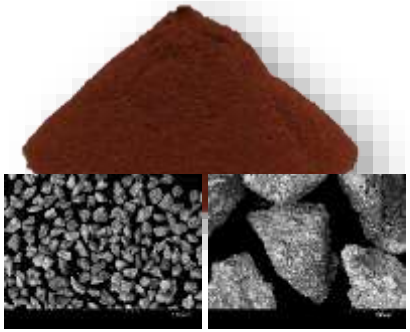
- ✓ Thermodynamic suitability
- ✓ High redox reactivity
- ✓ Sufficient oxygen transport capacity
- ✓ Resistance to attrition (lifetime)
- ✓ Low tendency for agglomeration
- ✓ Complete conversion to CO_2 and H_2O
- ✓ Negligible carbon deposition
- ✓ Environmentally friendly
- ✓ Low cost (production and operation)
- ✓ Resistant to sulphur

Synthetic

Metal Oxide
+
Support

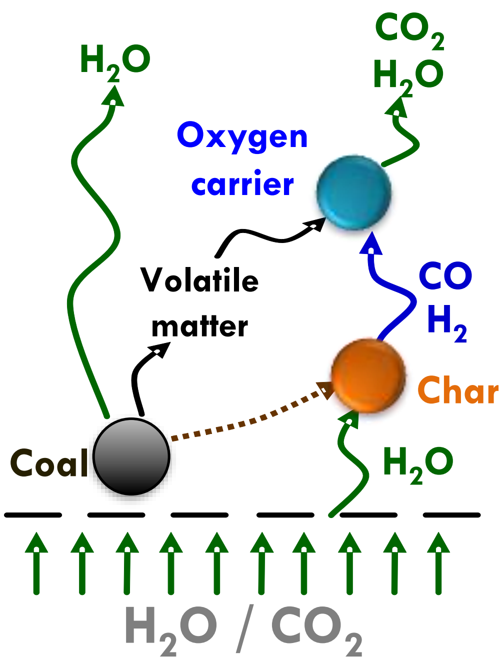


Minerals or wastes based on Fe, Mn



CLC options for solid fuels

in-situ gasification CLC (*i*G-CLC)



1. Coal is dried and devolatized

$$\text{Coal} \longrightarrow H_2O + \text{Volatile matter} + \text{Char}$$

2. Remaining solid char is gasified to give H_2 + CO

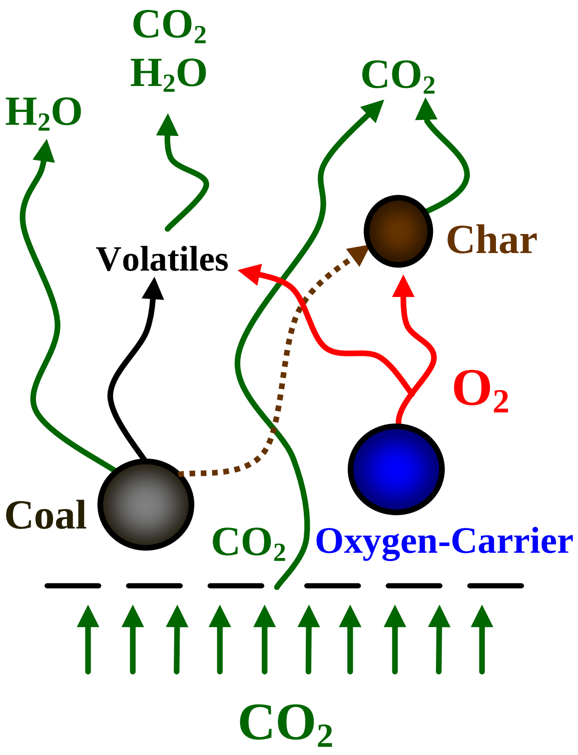
$$\text{Char} + H_2O \longrightarrow H_2 + CO$$

$$\text{Char} + CO_2 \longrightarrow 2\,CO$$

3. Volatiles and gasification products react with oxygen carrier by a gas-solid reaction

$$\begin{matrix}\text{Volatile matter}\\ H_2 + CO\end{matrix} + n\,Me_xO_y \longrightarrow CO_2 + H_2O + n\,Me_xO_{y-1}$$

Chemical Looping with Oxygen Uncoupling (CLOU)



1. Coal is dried and devolatized

$$\text{Coal} \longrightarrow H_2O + \text{Volatile matter} + \text{Char}$$

2. Oxygen-carrier with capacity to release gaseous OXYGEN (O_2)

$$2\,Me_xO_y \longrightarrow 2\,Me_xO_{y-1} + O_2$$

3. Volatiles and Char react with OXYGEN (O_2) as in common combustion with air

$$\begin{matrix}\text{Volatile matter}\\ \text{Char}\end{matrix} + O_2 \longrightarrow CO_2 + H_2O$$

CLC options for solid fuels

Key properties Oxygen carriers

iG-CLC

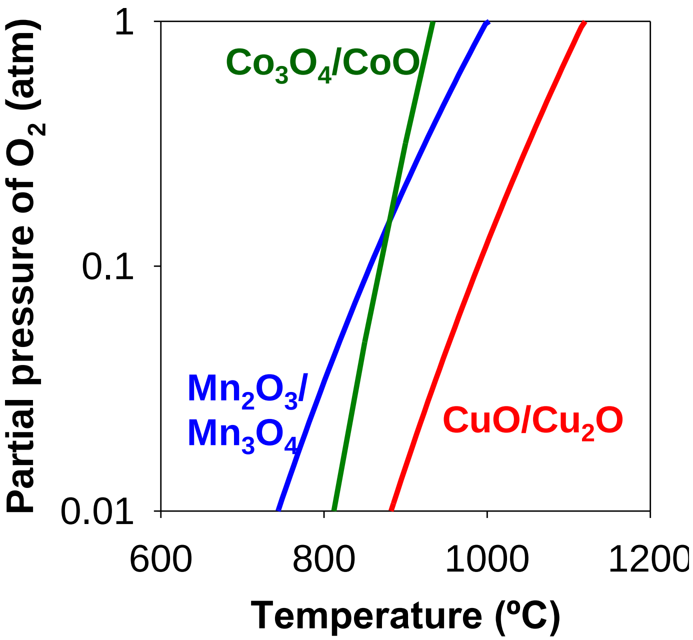
- OC reactivity is not a key factor because char gasification is a slow reaction
- Low cost material are very interesting

Natural ores and waste materials

Iron based OC	*Fe_2O_3/Fe_3O_4*
Ilmenite Iron ores Bauxite residues Industrial wastes	
Manganese ores	*Mn_3O_4/MnO*
Anhidrite ($CaSO_4$)	$CaSO_4/CaS$

CLOU

- Appropriate thermodynamic for oxygen uncoupling at temperature of interest
- Metal oxides – Cu, Mn, Co
- Mixed oxides – $CaMnO_3$, Cu-Mn, Mn-Fe



Objective

The objective of this work is to analyse the **performance of different oxygen carries** on the CLC process

- 8 different materials ranging from **iG-CLC to CLOU** properties
- Coal combustion in a **1.5 kW continuous CLC unit**

- Experiments were conducted in the 1.5 kWth continuously operated plant at ICB-CSIC where operating conditions were varied: temperature, solids inventory in the fuel reactor, solids circulation rate.
- The effect on the carbon capture efficiency and the oxygen demand of the process were analysed.

Experimental

Low Cost OCs ⟷ iG-CLC

Natural Minerals and Industrial Residues

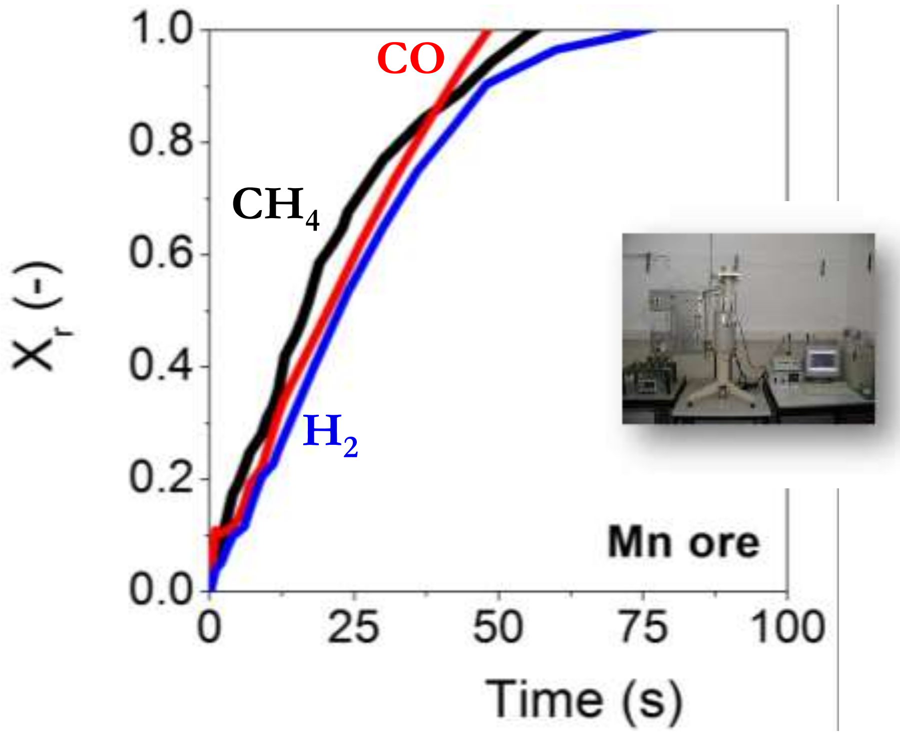
Oxygen carrier	Thermal treatment (°C/h)	Active phase Composition	R_{OC} (wt.%)	Porosity (%)	BET area (m^2/gr)	Crushing Strengh (N)
Ilmenite	950 / 24	55% Fe_2TiO_5 10% Fe_2O_3	4.0	1.2	0.8	2.2
Bauxite waste (Redmud)	1200 / 18	71% Fe_2O_3	2.0	10	0.1	2.8
Tierga Iron Ore	950 / 12	76% Fe_2O_3	2.0	25.4	1	4.6
Gabon Mn ore	800 / 2	68% Mn_3O_4 10.6% Fe_2O_3	5.0	38.7	12	1.8

All materials crushed and sieved to 100-300 µm

Materials characterization

Reactivity tests in TGA at 950 ºC

- 5% H_2 + 40% H_2O
- 15% CO + 20% CO_2
- 15% CH_4 + 20% H_2O
- 21% O_2



Rate index (%/min) from TGA tests at 950ºC

	CH_4	CO	H_2	O_2
Ilmenite	5.0	2.5	7.9	**9.7**
Redmud	3.4	3.9	10.5	4.1
Tierga Fe-ore	3.3	3.4	12.4	5.5
Mn ore	**9.2**	**6.4**	**19.2**	8.6

Mn ore has the highest oxygen transport capacity and the highest *rate index* than other Fe-based materials

Experimental

Low Cost OCs ⟷ iG-CLC+CLOU ⟷ CLaOU

Synthetic Mn-Fe mixed oxides

CLaOU = Chemical Looping Combustion assisted by Oxygen Uncoupling

Combustion of fuel by iG-CLC + limited CLOU behaviour that allows to reduce unburnt gases

Oxygen carrier preparation

- Mn_3O_4 (77 %) + Fe_2O_3 (24 %) $(Mn_{0.77}Fe_{0.23})_3O_4$
- Mn_3O_4 (60 %) + Fe_2O_3 (33 %) + TiO_2 (7 %) $(Mn_{0.66}Fe_{0.34})_2Ti_{0.15}O_{3.3}$

Spray drying + calcination (2 hours 1350 °C or 1200 °C with Ti)

TiO_2 addition to increase mechanical strenght of the oxygen carrier

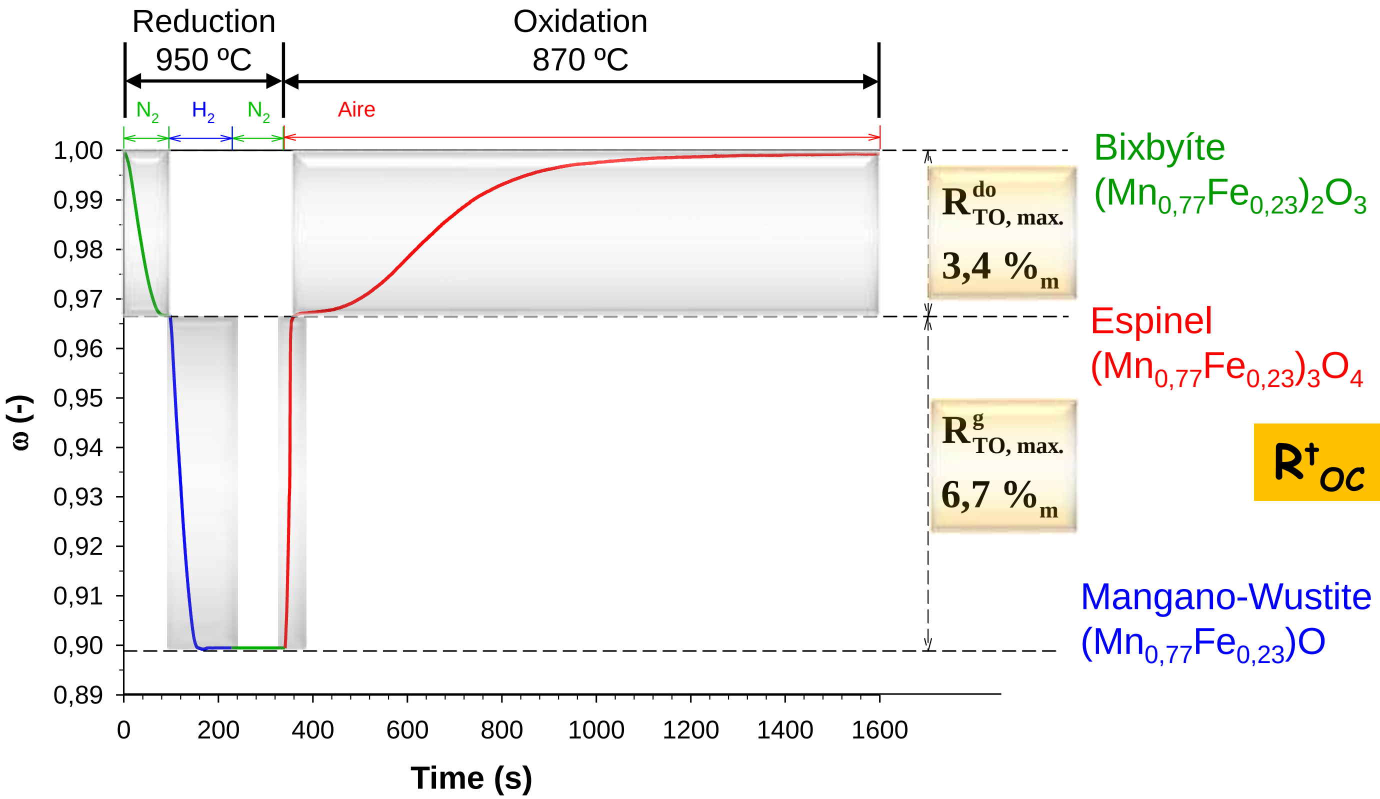
Experimental

		Mn77Fe[SD1350]	Mn66FeTi7[SD1200]
Sintering conditions	Time (h)	4 + 2	4 + 2
	Temperature (ºC)	950 + 1350	950 + 1200
Crushing strength (N)		1.7	2.0
XRD main phases (%)	$(Mn_xFe_{1-x})_2O_3$	13.6	81.0
	$(Mn_xFe_{1-x})_3O_4$	86.4	13.4
	TiO_2	-	5.6
Amorphous (%)		20	24
Relative permeability, K_m (-)		2.5	1.6

Magnetic properties for recovery from ashes

Mn66FeTi7 (SD1200)

Materials characterization



$R^{t}_{OC} = R^{clc}_{OC} + R^{clou}_{OC}$

$6\ (Mn_xFe_{1-x})_2O_3 \rightarrow 4\ (Mn_xFe_{1-x})_3O_4 + O_2$ → CLOU red. mechanism

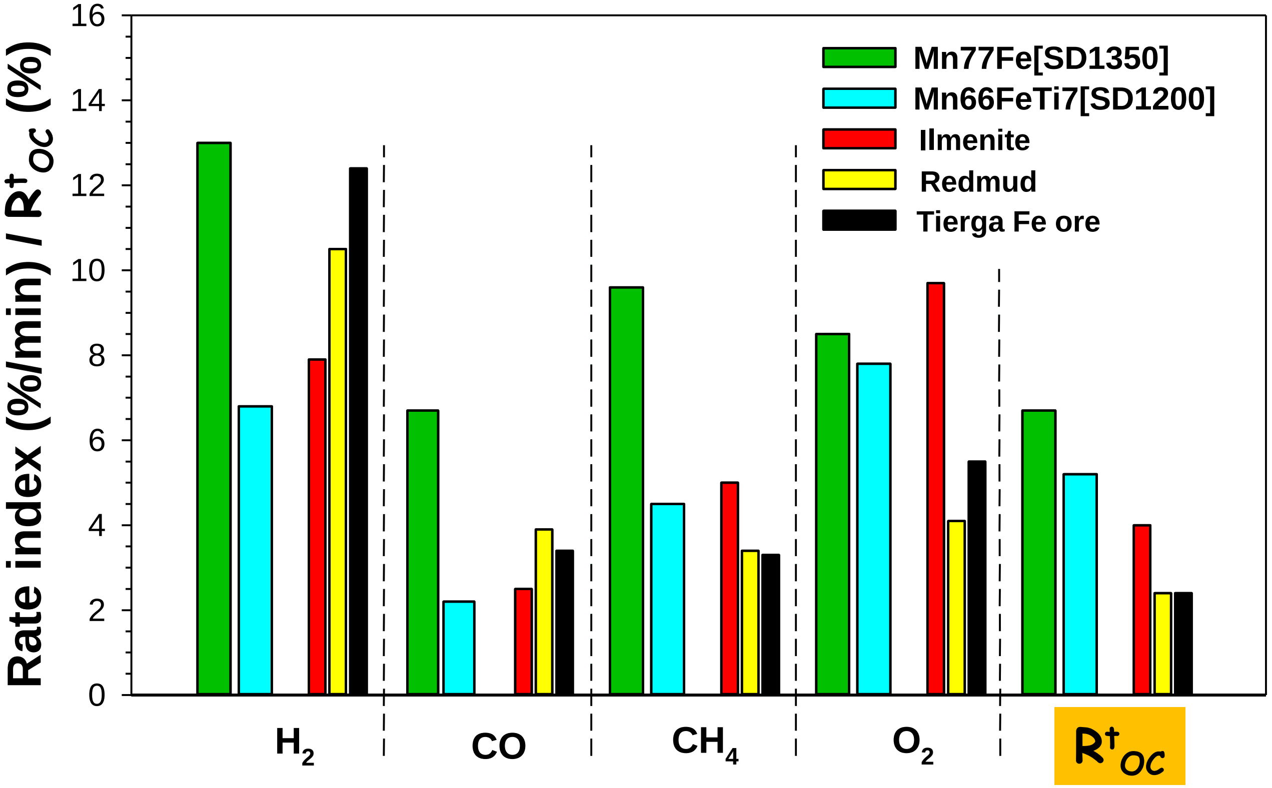
$(Mn_xFe_{1-x})_3O_4 + H_2 \rightarrow 3\ (Mn_xFe_{1-x})O + H_2O$ → CLC red. mechanism

$6\ (Mn_xFe_{1-x})O + O_2 \rightarrow 2\ (Mn_xFe_{1-x})_3O_4$ → CLC oxid. mechanism

$4\ (Mn_xFe_{1-x})_3O_4 + O_2 \rightarrow 6\ (Mn_xFe_{1-x})_2O_3$ → CLOU oxid. mechanism

Materials characterization

Rate indexes of low cost oxygen carriers



Mn77Fe[SD1350] has highest oxygen transport capacity and reactivity.

High Cost OCs ⟷ CLOU

Synthetic Cu-based oxides

Oxygen Carrier	Cu60MgAl	Cu34Mn66
Preparation method	Spray Drying	Granulation
Composition	60 % CuO 40% $MgAl_2O_4$	66.6 % Mn_3O_4, 33.3 % CuO
XRD main phases	CuO $MgAl_2O_4$	$Cu_{1.5}Mn_{1.5}O_4$ Mn_3O_4
Oxygen capacity (%)	6.0	4.0
Particle size (μm)	100-250	100-300
Crushing strength (N)	2.4	1.9

Fluidized Bed Granulator

Cu60MgAl ⇨ $\boxed{2\,CuO \longleftrightarrow Cu_2O + 0.5\,O_2}$

Cu34Mn66 ⇨ $\boxed{2\,Cu_{1.5}Mn_{1.5}O_4 \longleftrightarrow 3\,CuMnO_2 + O_2}$

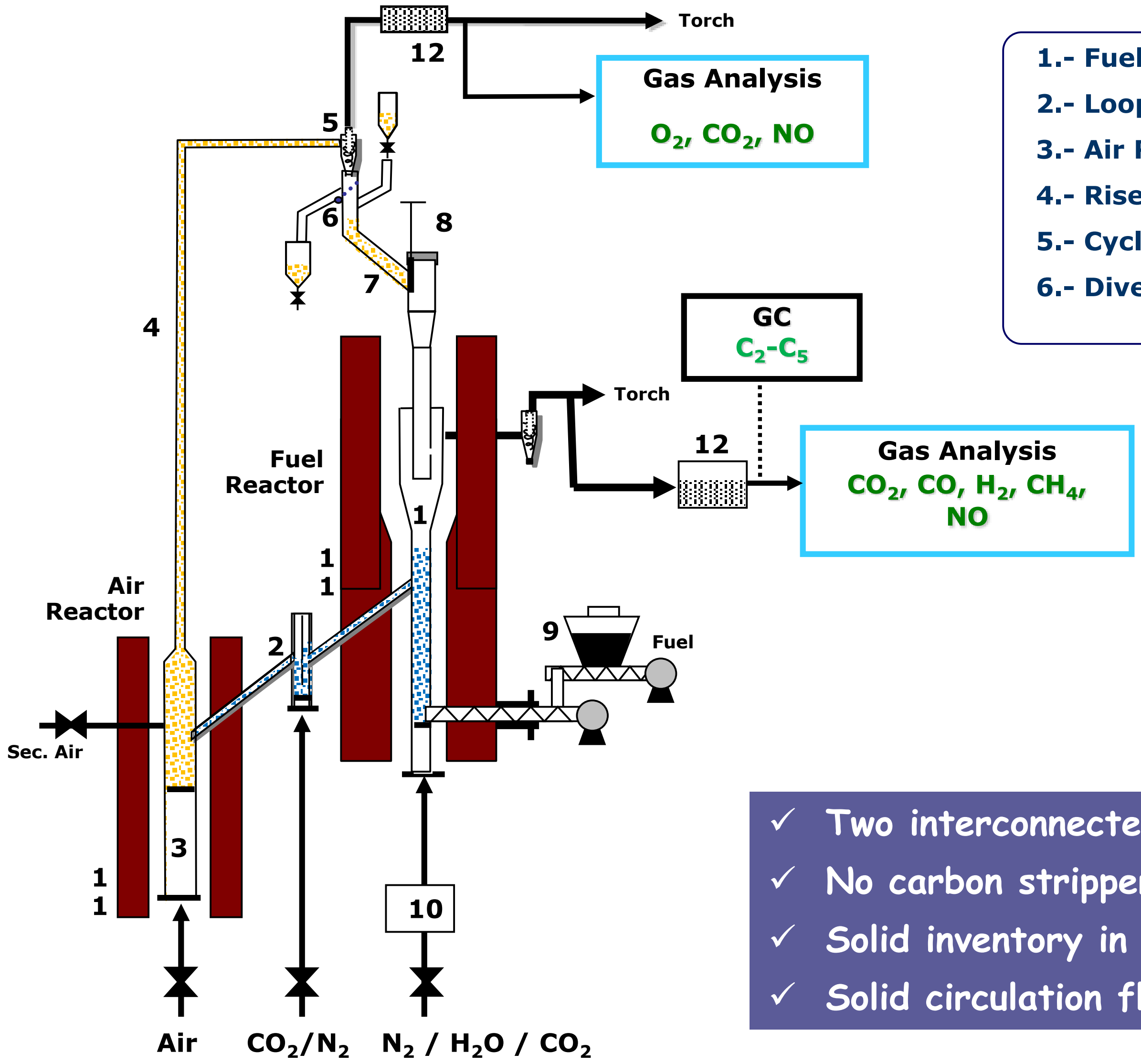
Coals

	Anthracite	LV Bitum.	MV Bitum_Russia	MV Bitum. South african	HV Bitum. Pretreated	Subbitum. Chile	Lignite Spain
Proximate analysis (wt %)							
Moisture	1.0	2.0	5.8	4.2	2.3	14.2	12.6
Volatile	7.5	17.1	32.0	25.5	33.0	34.6	28.6
Fixed carbon	59.9	68.8	52.1	55.9	55.9	35.9	33.6
Ash	31.6	12.1	10.1	14.4	8.8	15.3	25.2
Ultimate analysis (wt %)							
C	60.7	75.8	65.8	69.3	65.8	52.4	45.4
H	2.1	3.7	4.6	3.9	3.3	5.24	2.5
N	0.9	1.9	2.0	1.9	1.6	0.77	0.6
S	1.3	0.4	0.5	0.9	0.6	0.2	5.2
O*	2.4	4.1	11.3	5.4	17.6	11.9	8.5
LHV (kJ/kg)	21900	28950	26600	25500	21900	18900	16250

* by difference

Particle size +200 – 300 μm

0.5 kW_{th} iG-CLC /1.5 kW_{th} CLOU unit



- **1.- Fuel Reactor** (i.d.: 5 cm)
- **2.- Loop Seal**
- **3.- Air Reactor** (i.d.: 8 cm)
- **4.- Riser**
- **5.- Cyclone**
- **6.- Diverting solids valve**
- **7.- Solid reservoir**
- **8.- Solids control valve**
- **9.- Fuel feeding system**
- **10.- Evaporator**
- **11.- Furnace**
- **12.- Filter**

- ✓ Two interconnected bubbling fluidized bed reactors
- ✓ No carbon stripper
- ✓ Solid inventory in the FR measured from ΔP
- ✓ Solid circulation flow rate measured from a valve

Experimental

Operating conditions in the CLC unit

	iG-CLC	CLaOU	CLOU
Hours of combustion (fuel feeding)	300	85	200
Solids inventory in FR (kg/MW_{th})	1000-2000	850-1500	500-1000
FR Fluidizing agent	H_2O/CO_2	N_2	N_2
FR temperature (ºC)	890-955	900-950	800-960
AR temperature (ºC)	950	800-950	800-900

Data Evaluation

$$\phi = \frac{\text{Oxygen in oxygen carrier}}{\text{Oxygen to burn fuel}}$$

Total oxygen demand

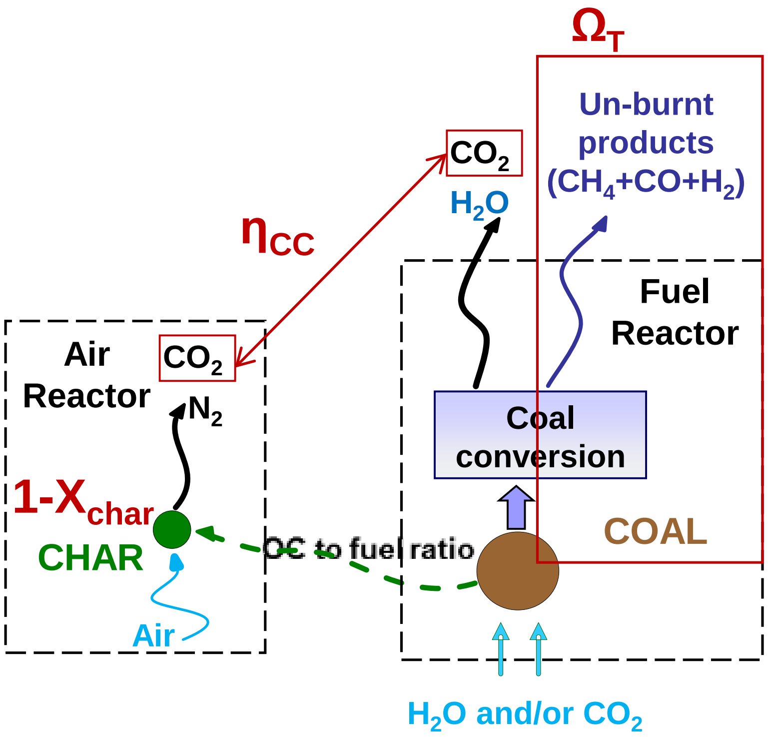
$$\Omega_T = \frac{\text{Ox. required combustion of unburnt products}}{\text{Ox. Required for complete combustion of biomass}}$$

CO_2 capture efficiency

$$\eta_{CC} = \frac{\text{Carbon converted to gas in the FR}}{\text{Carbon introduced in the FR}}$$

Char conversion

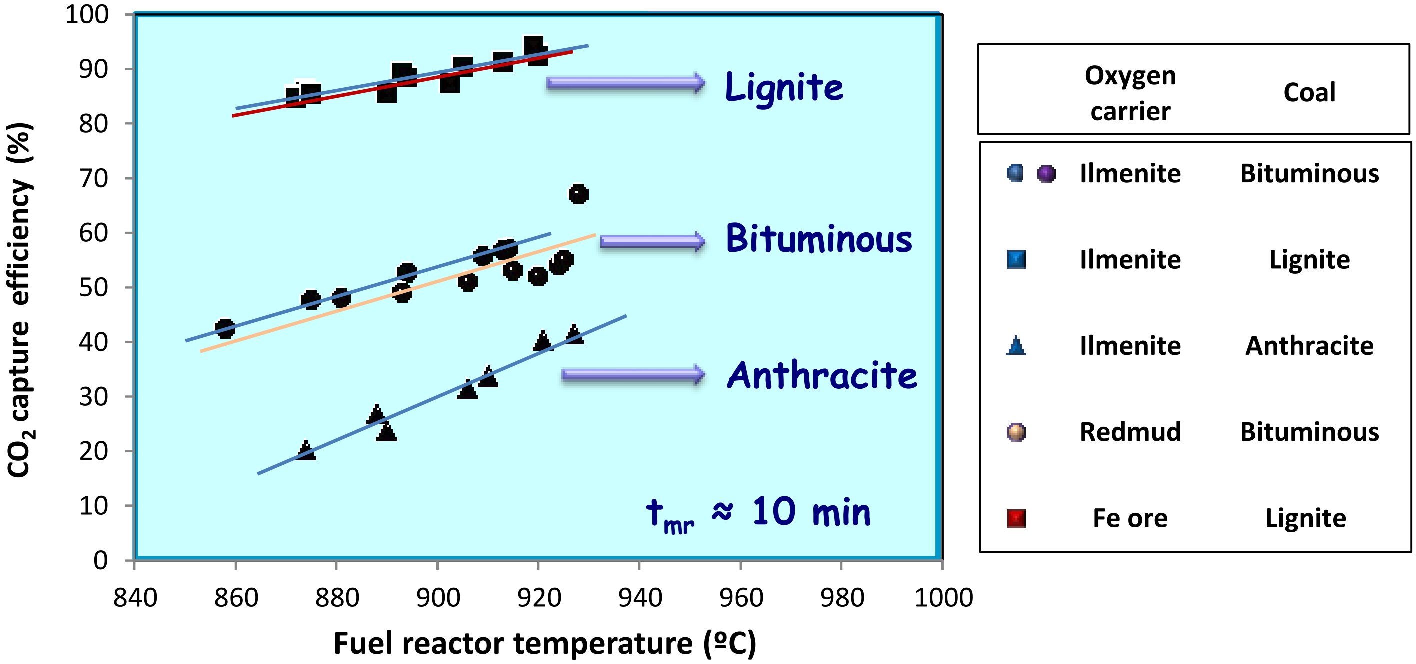
$$X_{char} = \frac{\text{Char gasified in the FR}}{\text{Char introduced with the fuel feed}}$$



Results on CO_2 Capture

Low Cost OCs ⟷ iG-CLC

Natural Minerals and Industrial Residues



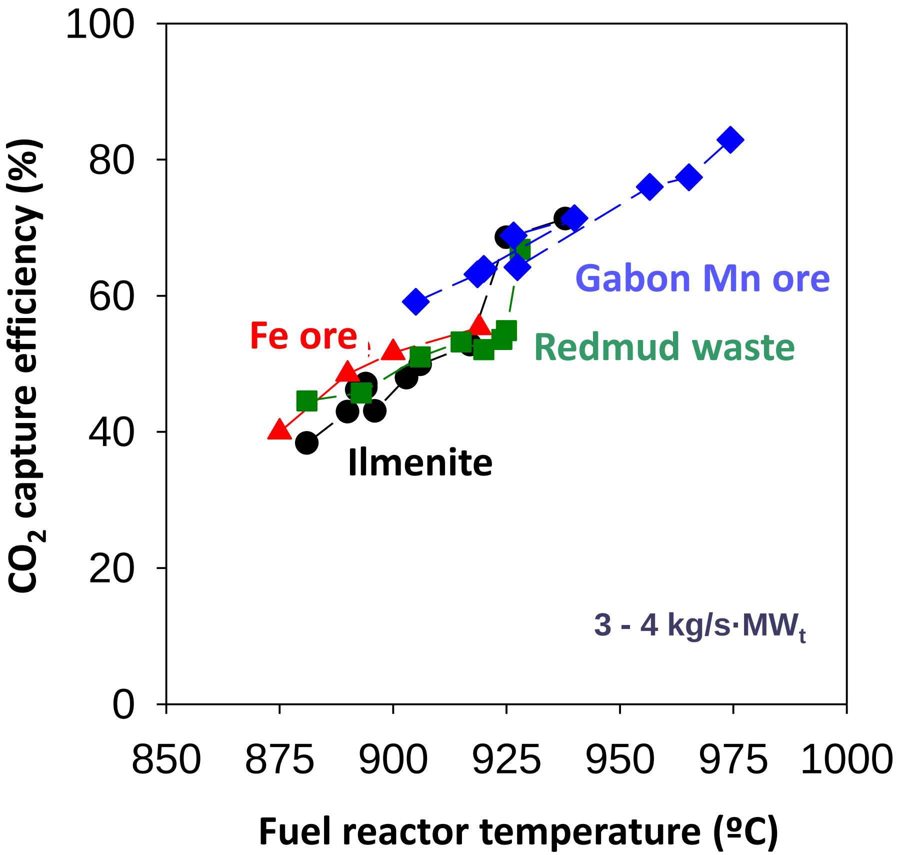
	Oxygen carrier	Coal
● ●	Ilmenite	Bituminous
■	Ilmenite	Lignite
▲	Ilmenite	Anthracite
●	Redmud	Bituminous
■	Fe ore	Lignite

- ✓ CO_2 capture increased with the coal reactivity: **Lignite > Bituminous > Anthracite**
- ✓ CO_2 capture increased with the FR temperature

Results on CO_2 Capture

Low Cost OCs iG-CLC

Natural Minerals and Industrial Residues

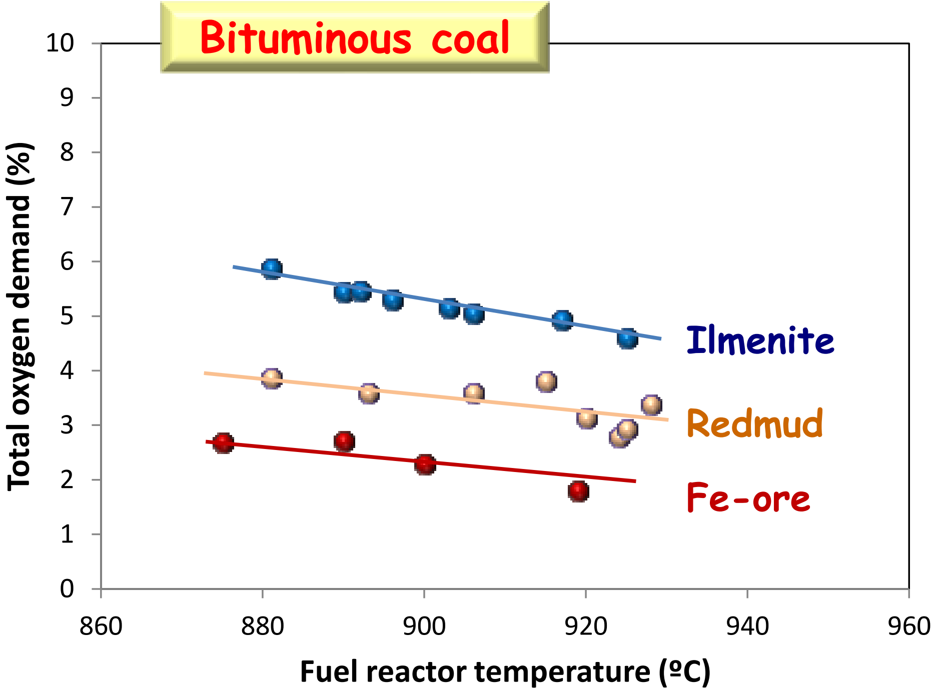


✓ The reactivity of the oxygen carrier barely affected to the CO_2 capture

Results on Oxygen Demand

Low Cost OCs ⟷ iG-CLC

Natural Minerals and Industrial Residues

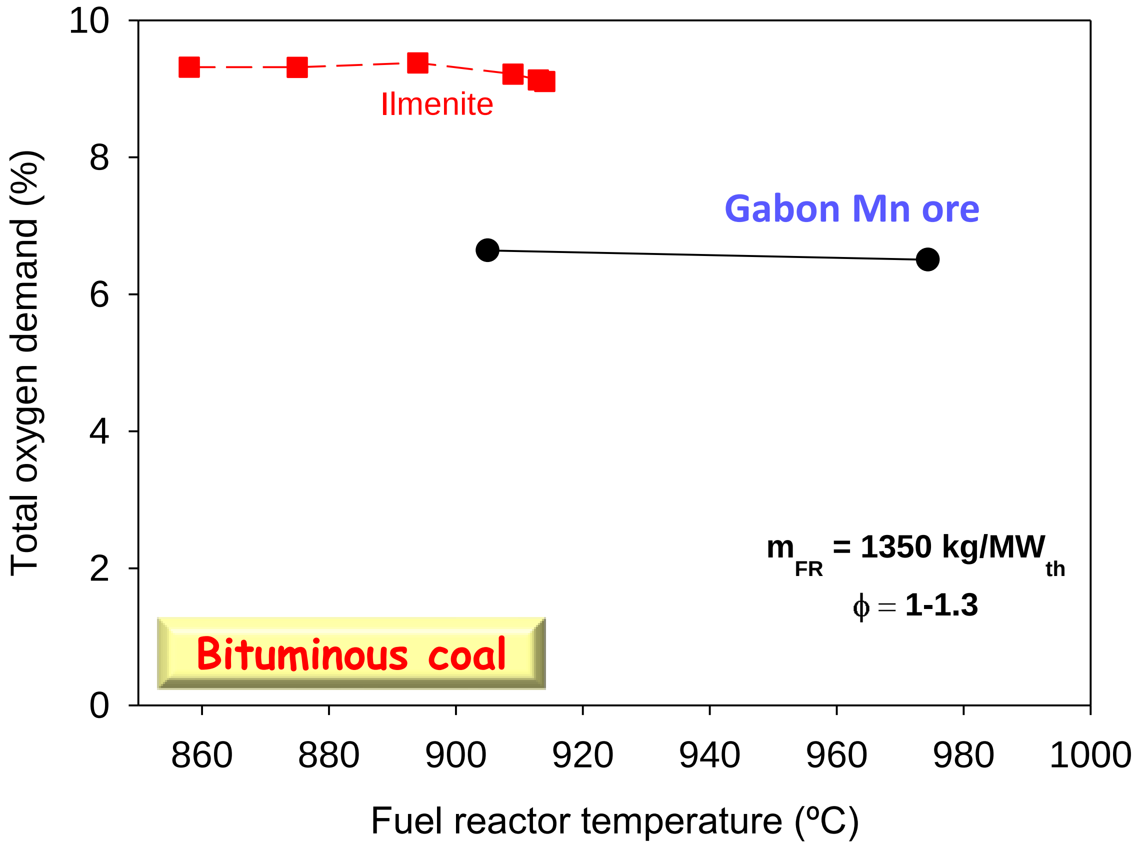


- ✓ The oxygen demand decreased by using more reactive oxygen carriers.

Results on Oxygen Demand

Low Cost OCs ⟺ iG-CLC

Natural Minerals and Industrial Residues

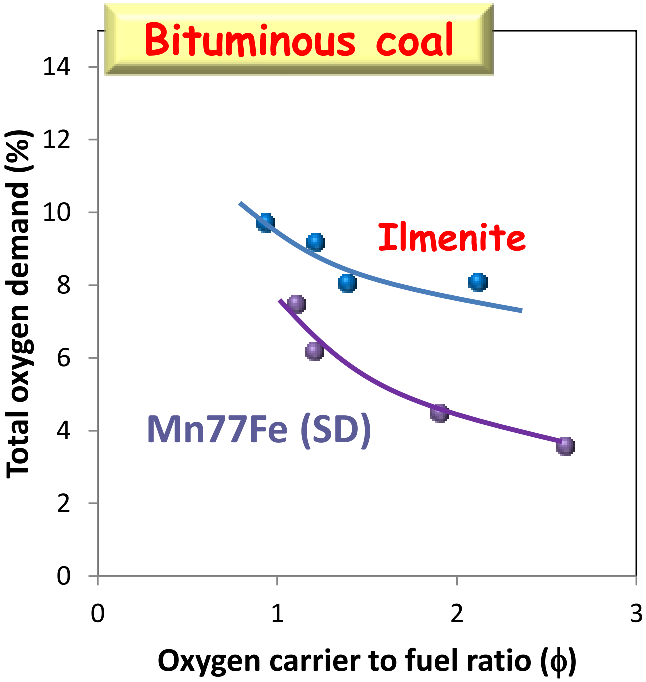


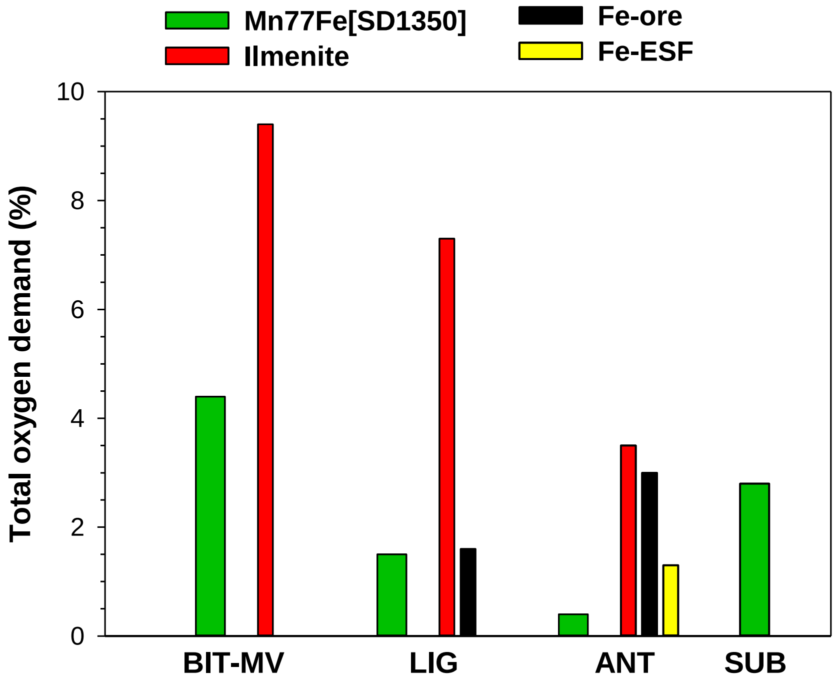
✓ The oxygen demand decreased by using more reactive oxygen carriers.

Results on Oxygen Demand

Low Cost OCs ⟷ iG-CLC+CLOU ⟷ CLaOU

Synthetic Mn-Fe mixed oxides



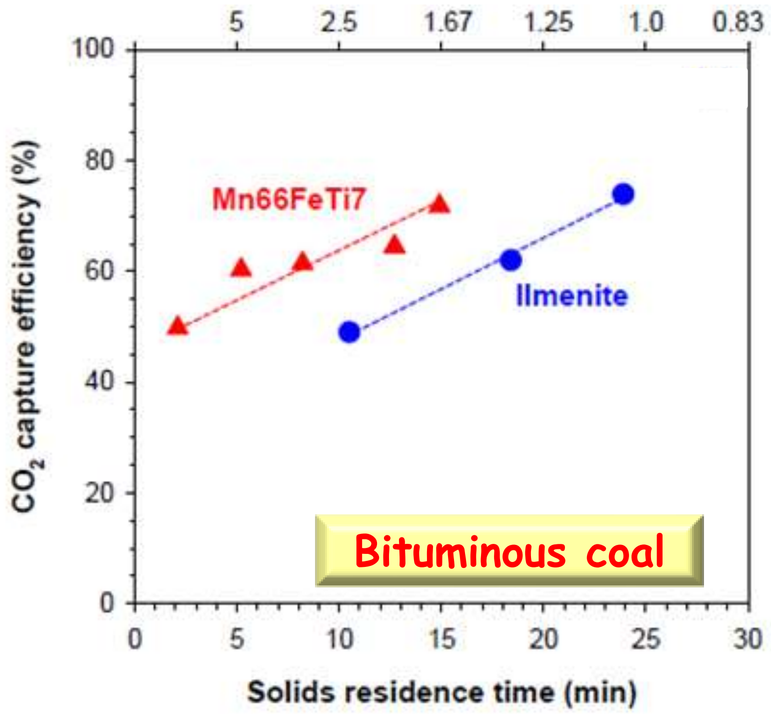


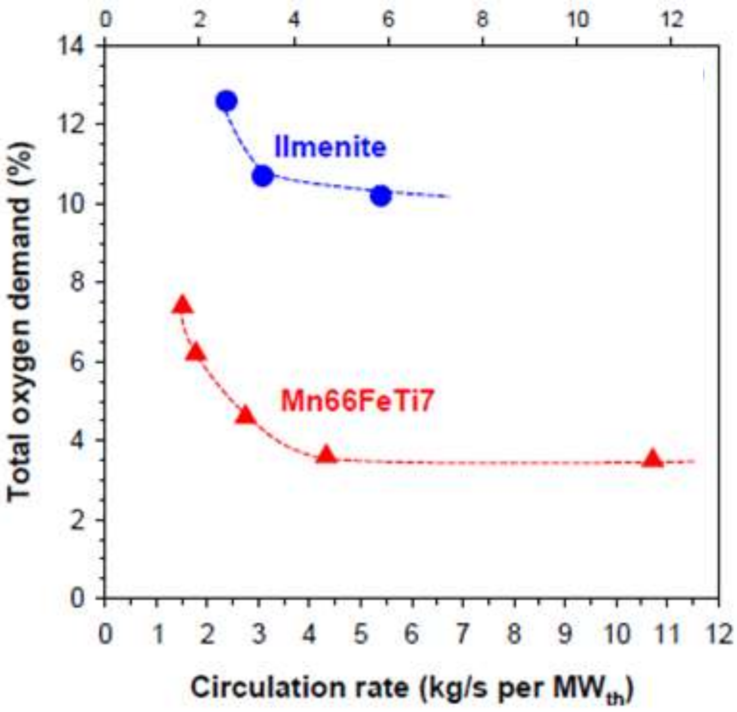
- ✓ *Synthetic low cost materials showed an important improvement of the CLC performance.*

Results on Oxygen Demand

Low Cost OCs ⟷ iG-CLC+CLOU ⟷ CLaOU

Synthetic Mn-Fe mixed oxides



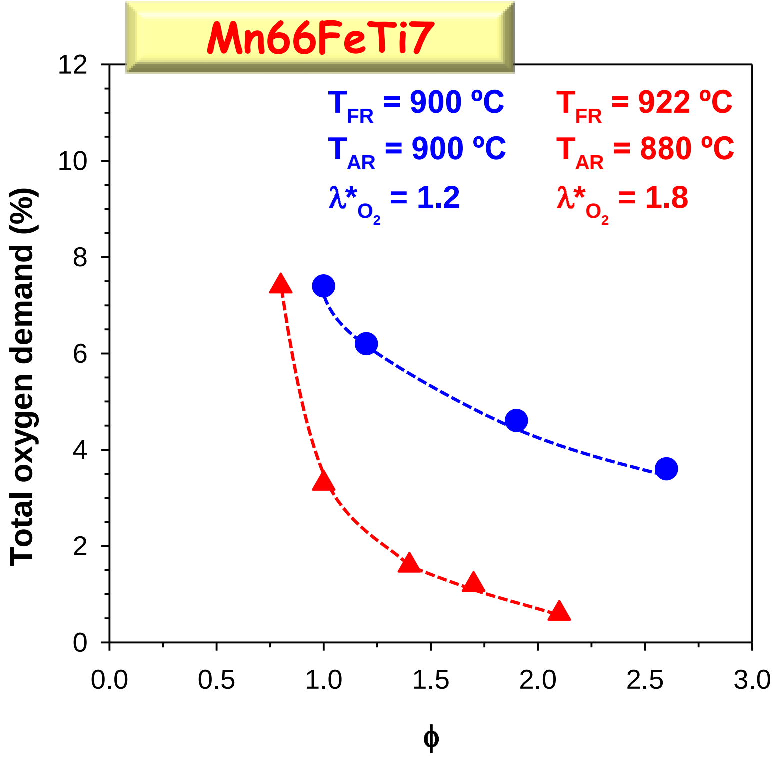


✓ Synthetic low cost materials with CLOU properties allowed to reduce unburnt gases.

Results on Oxygen Demand

Low Cost OCs ⟷ iG-CLC+CLOU ⟷ CLaOU

Synthetic Mn-Fe mixed oxides

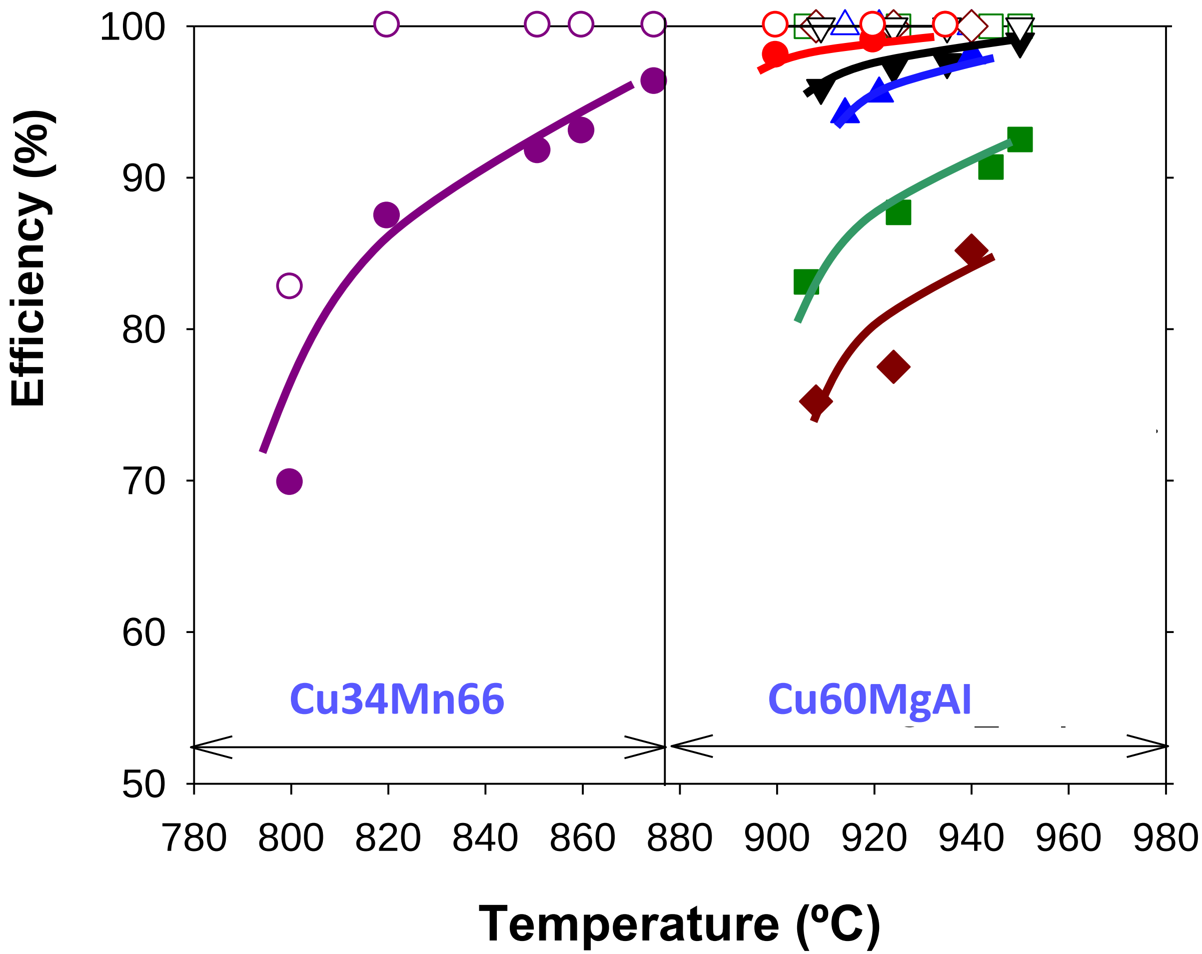


- ✓ Optimization of operating conditions allows to improve CLOU effect.
- ✓ Lowest oxygen demand (Ω_t =0.5 %) obtained with low cost oxygen carriers.

Results

High Cost OCs ⟷ CLOU

Synthetic Cu-based oxides



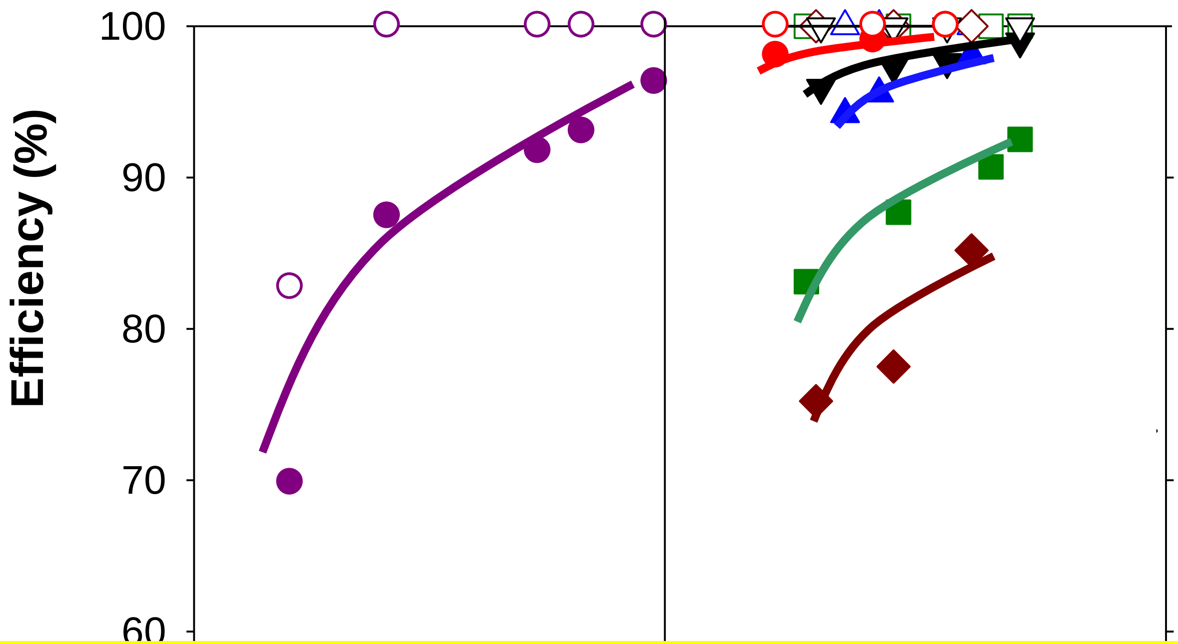
Fuel	Capture	Combustion
HVB	●	○
Lignite	▼	▽
Subbitum.	●	○
MVB	▲	△
LVB	■	□
Anthracite	◆	◇

Results

High Cost OCs ⟷ CLOU

Synthetic Cu-based oxides

Fuel	Capture	Combustion
HVB	●	○
Lignite	▼	▽
Subbitum.	●	○
MVB	▲	△
LVB	■	□
Anthracite	◆	◇



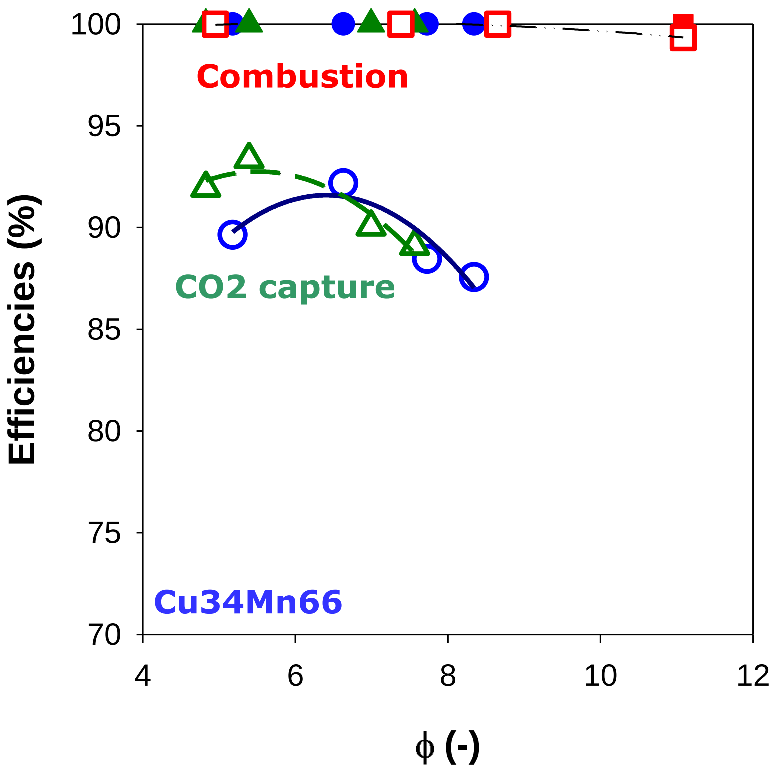
- ✓ CO_2 capture efficiency depends on FR temperature and coal reactivity.
- ✓ Zero oxygen demand (100% combustion efficiency) was obtained at temperatures > 800°C with CLOU oxygen carriers.

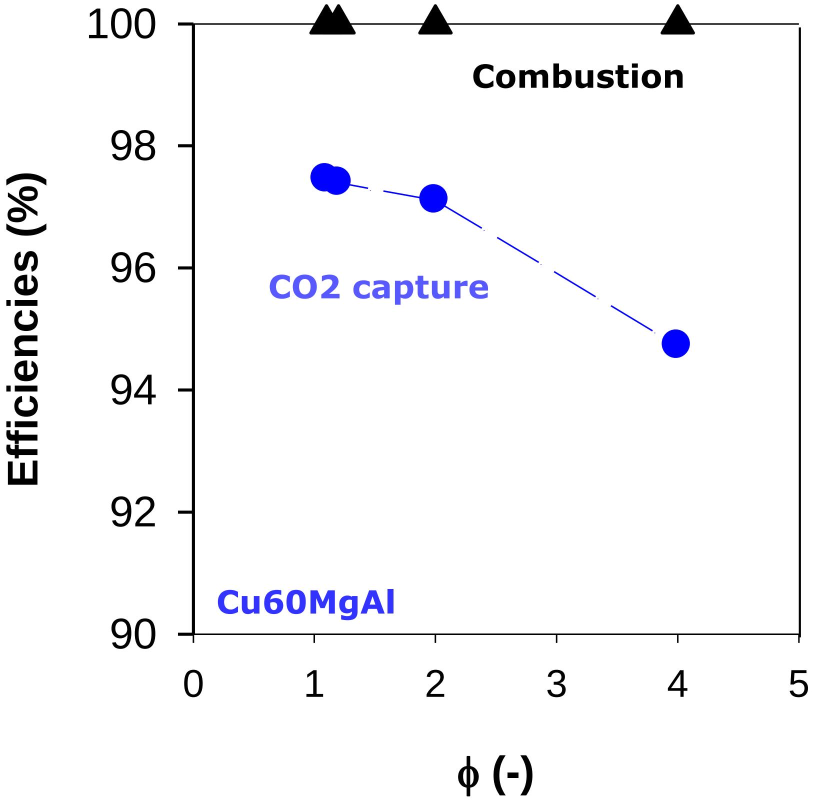
Results

High Cost OCs ⟷ CLOU

Synthetic Cu-based oxides

	Comb	Capture
Lignite	🟥	☐
MVB_SA	●	○
MVB_R	▲	△



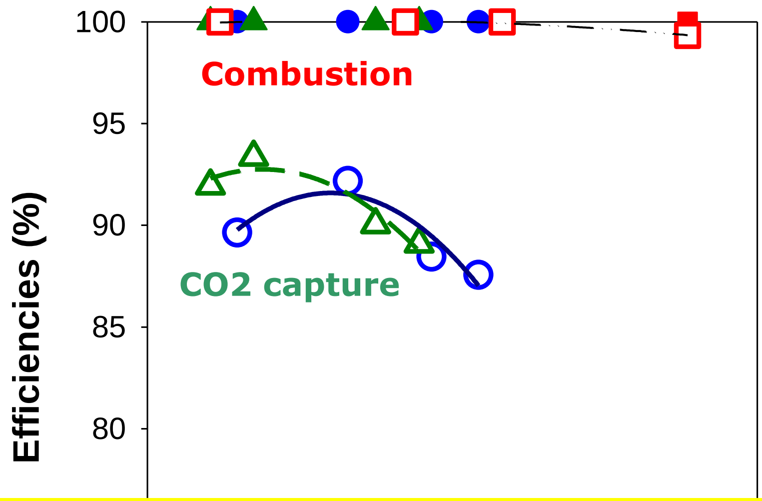


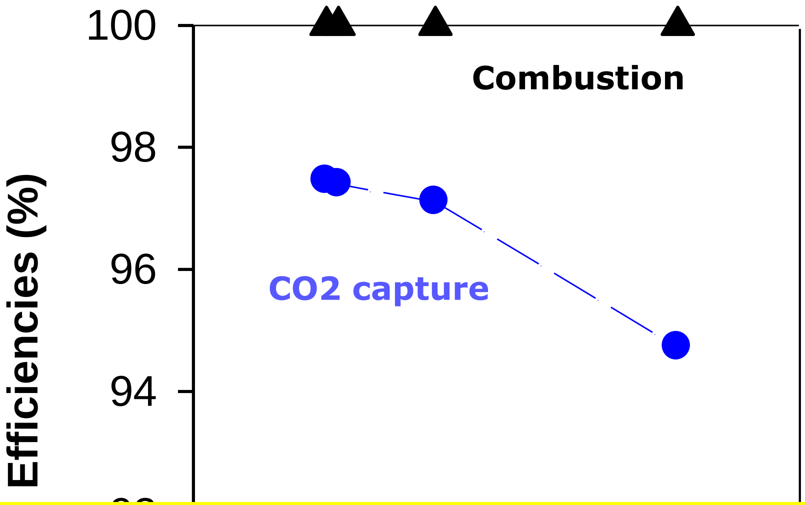
Results

High Cost OCs ⟷ CLOU

Synthetic Cu-based oxides

	Comb	Capture
Lignite	■	□
MVB_SA	●	○
MVB_R	▲	△





- ✓ CO_2 capture efficiency decreases with the increase of oxygen carrier to fuel ratio due to a decrease in the solid residence time.
- ✓ Full combustion efficiency was always obtained independently of the solid circulation rate for CLOU oxygen carriers.

Conclusions

Effect on CLC performance of the oxygen carrier reactivity and CLOU properties

- CO_2 capture efficiency mainly dependent on the coal char reactivity, and FR temperature

- The oxygen demand in iG-CLC decrease with the increase of oxygen carrier reactivity

  Mn ores > Fe ores > ilmenite

- Significant decrase of the oxygen demand by using oxygen carriers with CLaOU behaviour (combined CLC and limited CLOU)

  $(Fe_{0.34}Mn_{0.66})_2Ti_{0.15}O_{3.3}$ $\Omega_T = 0.5\ \%$

- When oxygen carriers with high oxygen generation rates (CLOU) are used ***oxygen demand is always cero using coals of any rank.***

  (Cu60MgAl) - $(Cu_{1.5}Mn_{1.5}O_4)$ $\Omega_T = 0$

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