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Assessment of Low-cost Oxygen Carrier in South-western Colombia, and its use in the *in-situ* Gasification Chemical Looping Combustion Technology

Francisco J. Velasco-Sarria, Carmen R. Forero, Iñaki Adánez-Rubiano, Alberto Abad, Juan Adánez

CSIC Consejo Superior de Investigaciones Científicas

Universidad del Valle

LCC Laboratorio Combustión Combustibles

icb Instituto de Carboquimica

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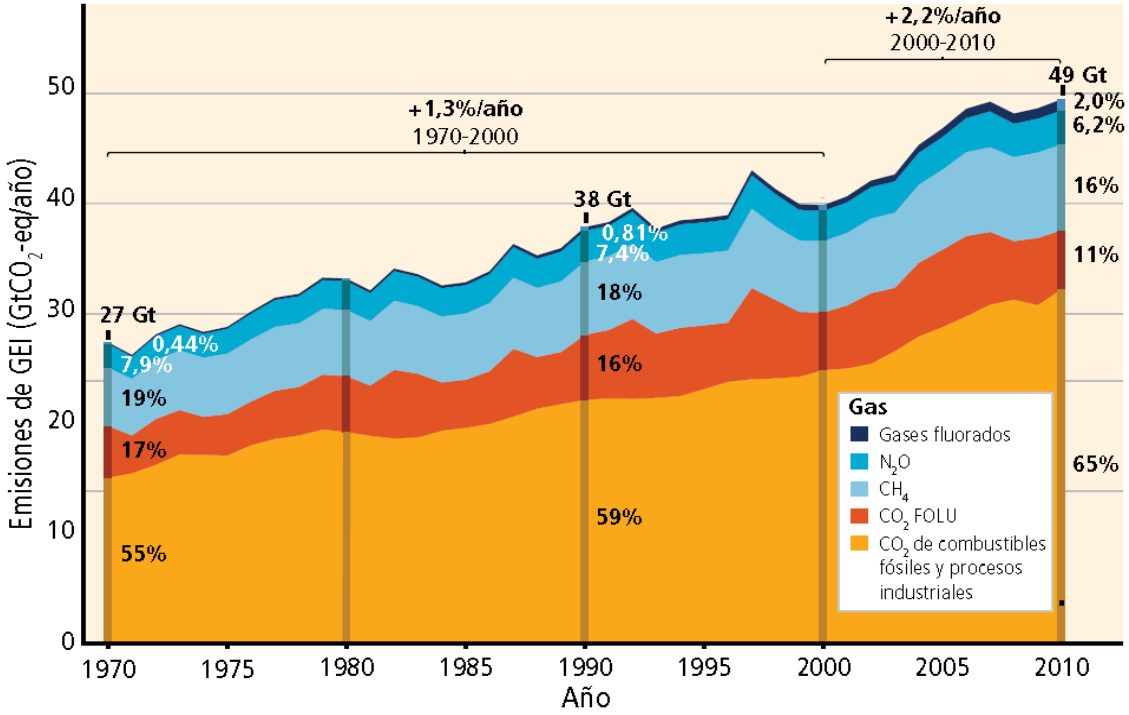
INTRODUCTION

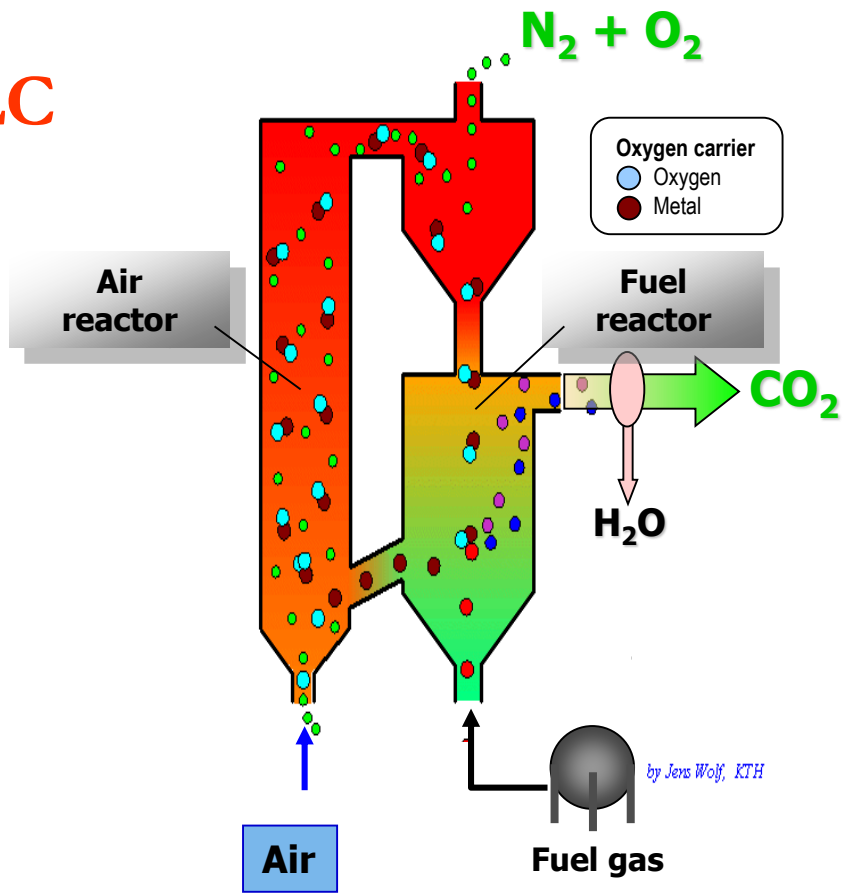


(IPCC, 2014)

- The current increase in greenhouse gas concentration is evident .
- CLC technology has emerged as an attractive option.
- Inherently removed

INTRODUCTION

CLC



- Divide the combustión.
- OC circulates
- CO_2 is not diluted
- Energy yield is the same CC.

- **Reduction:** Fuel + $Me_xO_y \rightarrow H_2O + CO_2 + Me_xO_{y-1}$
- **Oxidation:** $Me_xO_{y-1} + ½\ O_2 \rightarrow Me_xO_y$

GLOBAL: Fuel + $O_2 \rightarrow H_2O + CO_2$ $\quad \Delta H_{comb} = \Delta H_{red} + \Delta H_{ox}$

Low-cost oxygen carriers

- OC is the key.
- Several studies: find materials.
- Most studies: using active metal oxides, combined with an inert material .
- Nowadays: inexpensive materials to process solid or gaseous fuels.
- When solid fuels are used there are losses of OC
- Mn minerals are becoming important.

Mn in CLC and combined oxides

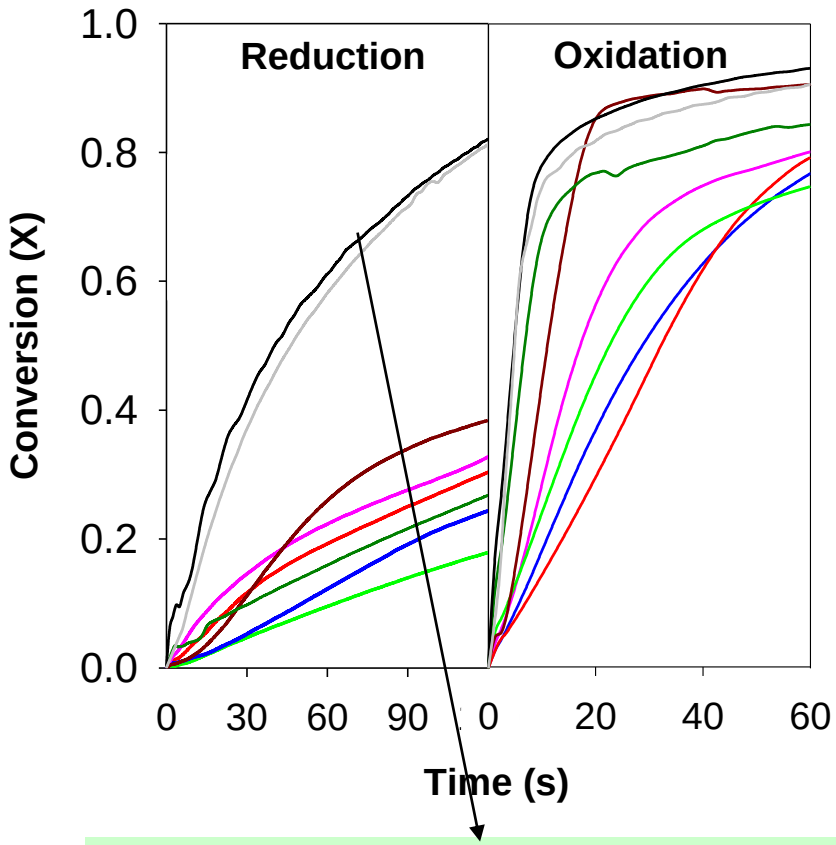
$2Mn_3O_4 \leftrightarrow 6MnO + O_2$ CLC

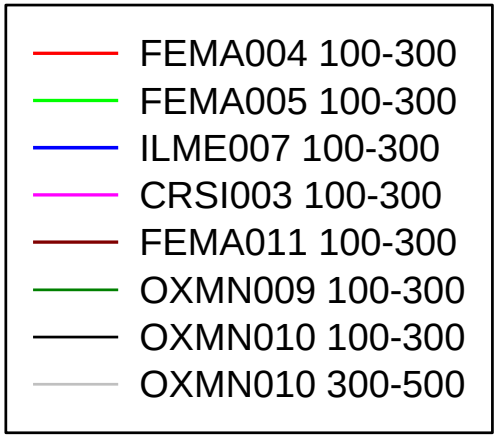
$6Mn_2O_3 \leftrightarrow 4Mn_3O_4 + O_2$ CLOU

- MnO_2 decomposes 500 °C
- Mn_3O_4 stable above 800 °C
- Mn_2O_3 may be an alternative
- Mn could form combines oxide for example rhodonite

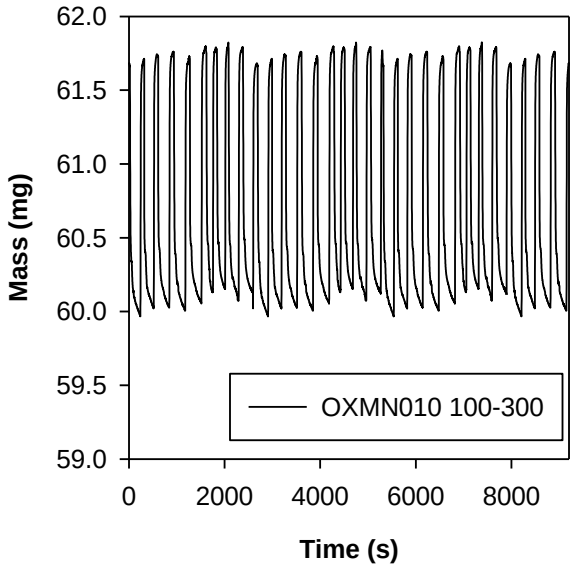
Sample	Reactive	Reactions
OXMN010 100-300	CH_4	$2Mn_7SiO_{12} + 12SiO_2 + \frac{3}{2}CH_4 \rightarrow 14MnSiO_3 + \frac{3}{2}CO_2 + 3H_2O$
	CO	$Mn_7SiO_{12} + 6SiO_2 + 3CO \rightarrow 7MnSiO_3 + 3CO_2$
	H_2	$Mn_7SiO_{12} + 6SiO_2 + 3H_2 \rightarrow 7MnSiO_3 + 3H_2O$
	O_2	$14MnSiO_3 + 3O_2 \rightarrow 2Mn_7SiO_{12} + 12SiO_2$

INTRODUCTION





OXMN010 100-300



Previous study

OBJETIVE

The objective of this work is to study the behaviour of a mineral of Mn (OXMN010 100-300) in a batch fluidized bed (bFB) with gaseous (CLC) and solid (iG-CLC) fuels.

METHODOLOGY

Mineral studied

Particle diameter (µm)	Oxygen transport capacity (% w/w)	Crushing strength (N)	Surface Area BET (m^2/g)	Elementary composition (XRF) [a]							Crystalline phases (XRD) [b]	
				Si	Al	Fe	Ca	Mg	Ti	Mn	MnSiO3 (Rodonite)	FeO (Wüstite)
100-300	3,4	2,3	23,3	13	2,5	3,5	1,9	0,8	0,2	35,7	85,4	6,1

- Sampling is performed according to the ASTM D2234 norm.
- The characterization.

Batch fluidized bed (bFB) with gas fuels - CLC

Fuel	%	N_2 to balance	Oxidant	%	N_2 to balance
CH_4	25	75	O_2	10	90
CO-CO_2	50-20	30	O_2	10	90
H_2	50	50	O_2	10	90

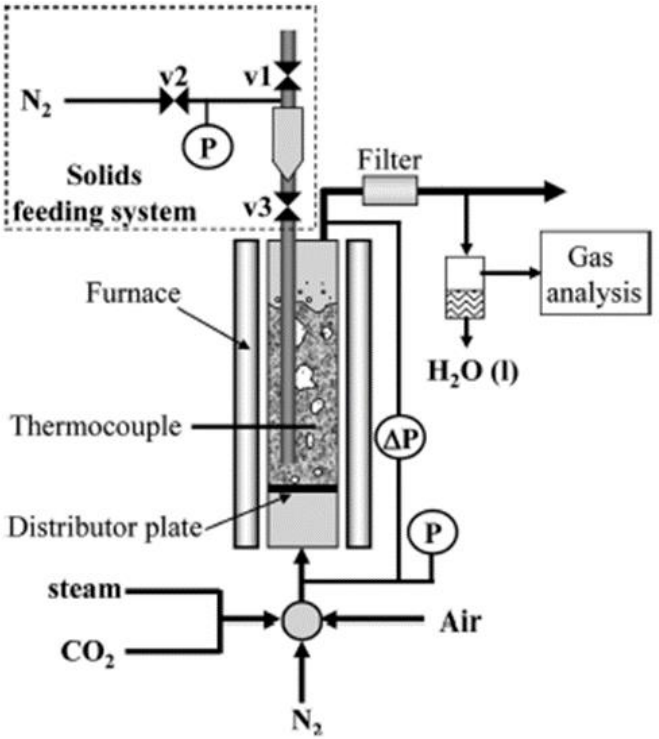
Q = 230 LN/h

T = 950 °C

tr = 60 s
to = 360 s for CO
480 s for H_2
600 s for CH_4
tp = 180 s.

Woc = 150 g

Vmf = 0,12 m/s (u/umf > 2.1).



CO, CO_2 H_2, O_2, CH_4

bFB with coal - *i*G-CLC

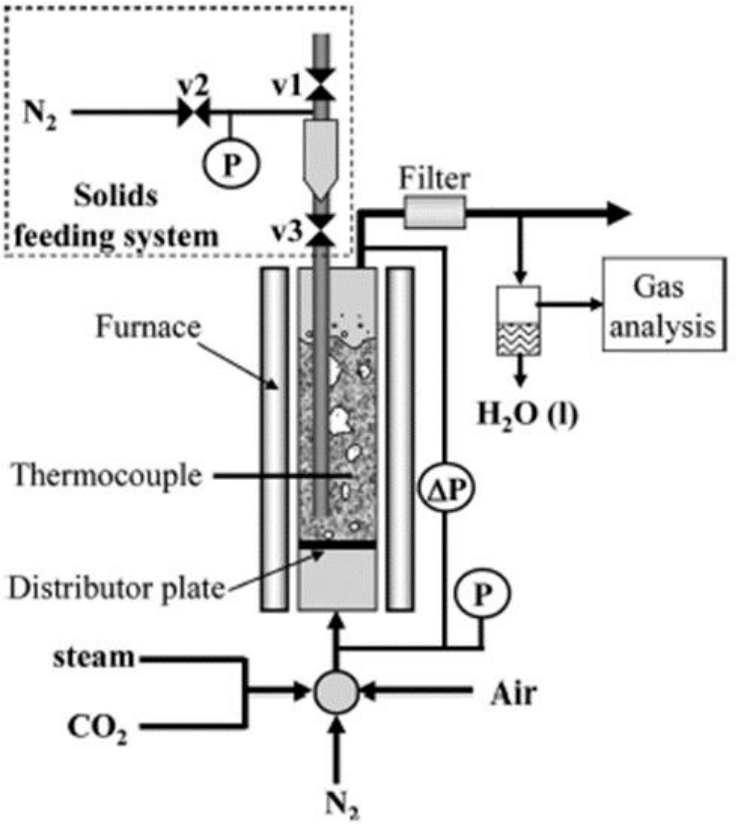
Q = 172 L_N/h

T = 900 °C, 950 °C
1000°C.

w_{coal} = 0,5 g :1,0 g :1,5 g
2,0 g : 2,5 g

w_{OC} =150 g

w_{sand} = 150 g (blak test)



CO, CO_2 H_2, O_2, CH_4

A subbituminous coal from Mina Invierno in Riesco Island (Chile)

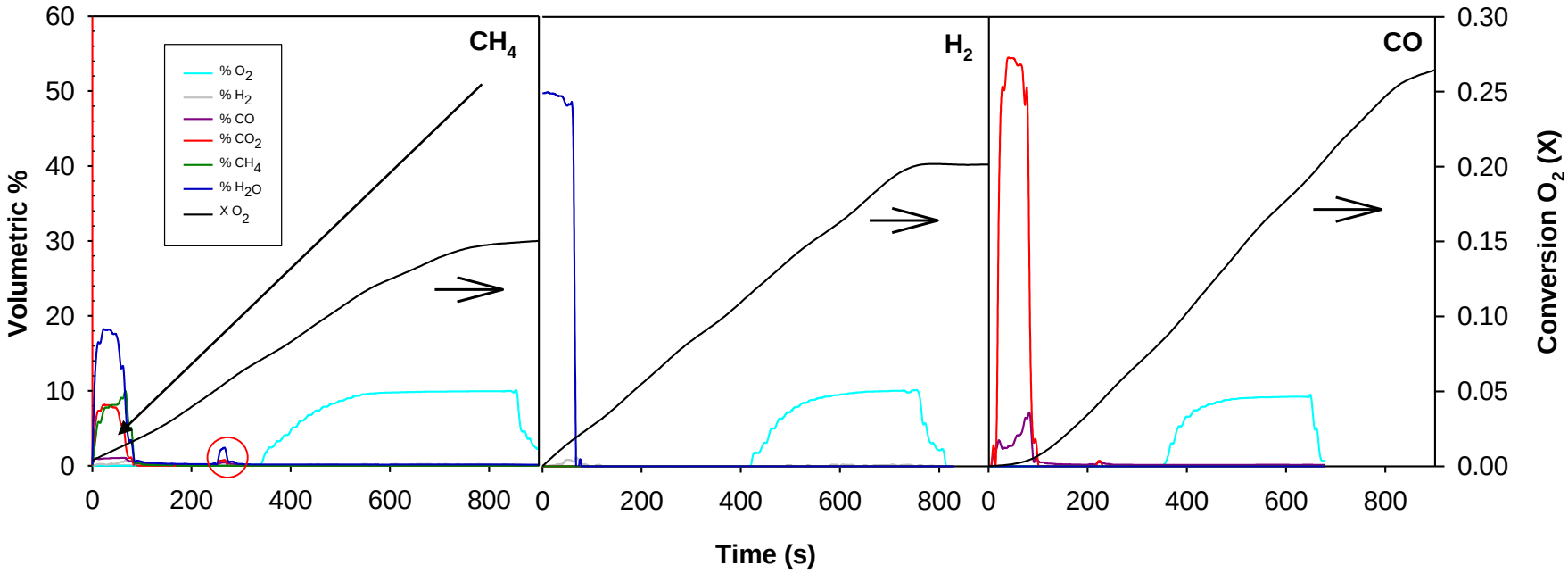
RESULTS

The characterizations of the sample

Particle diameter (μm)	Oxygen transport capacity (% w/w)	Crushing strength (N)	Surface Area BET (m^2/g)	Elementary composition (XRF) [a]							Crystalline phases (XRD) [b]	
				Si	Al	Fe	Ca	Mg	Ti	Mn	MnSiO3 (Rodonite)	FeO (Wüstite)
100-300	3,4	2,3	23,3	13	2,5	3,5	1,9	0,8	0,2	35,7	85,4	6,1

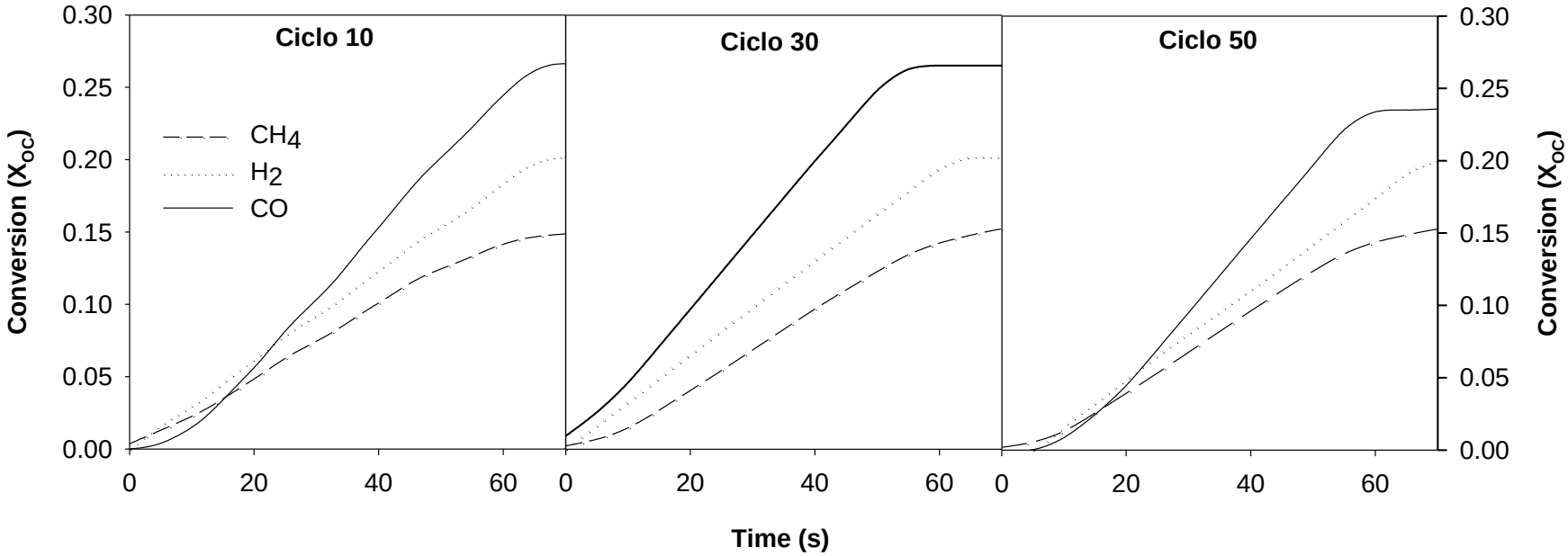
Thermally treated (heating at 1050° C for 4 hours with air at atmospheric pressure) ⟹ Crushing strength 3 N

Experiments in bFB with gaseous fuels (CLC)



Distribution of gaseous products during reduction, purging and oxidation in bFB with: CH_4 50%, H_2 25% and CO 25% at 950ºC.

Experiments in bFB with gaseous fuels (CLC)

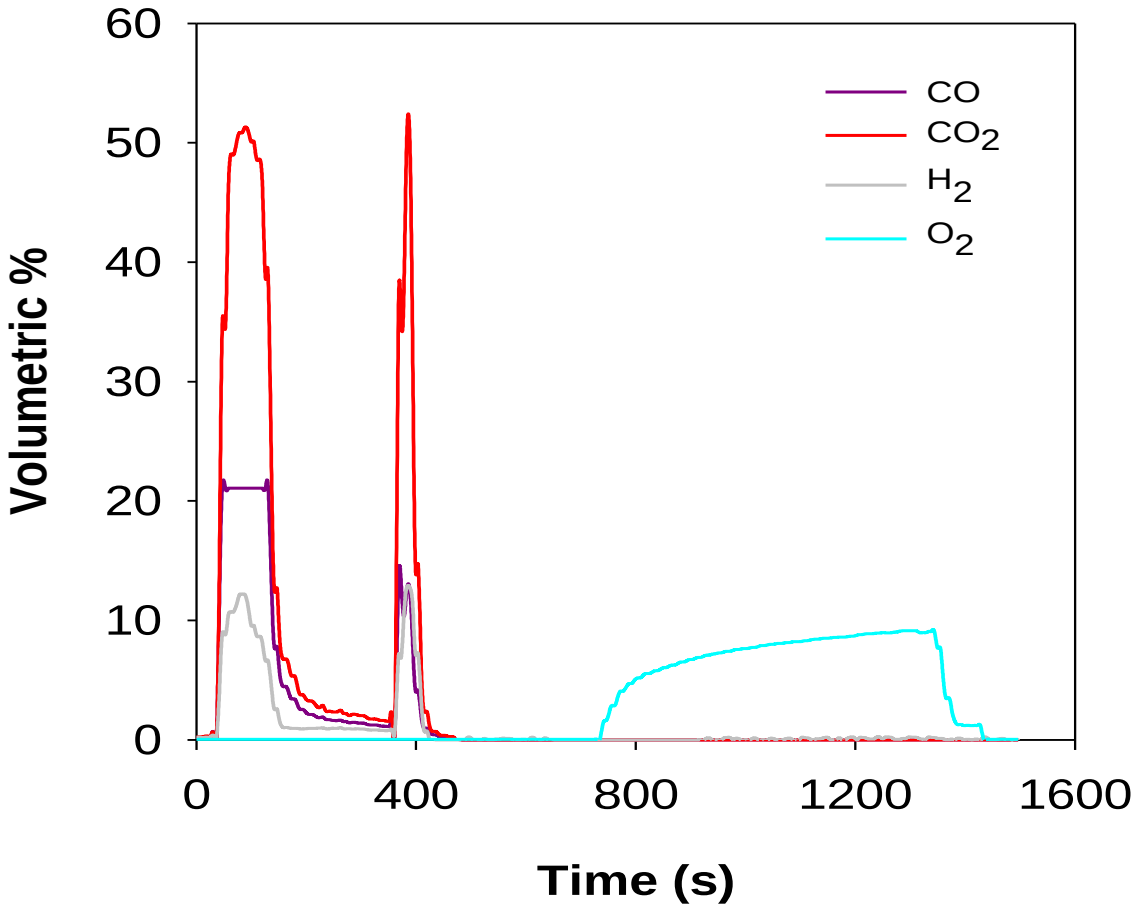


Oxygen conversion for OXMN010 100-300 at 950 ºC

$$X_{fuel}(t) = 1 - \frac{\int_{t_{r,0}}^{t} r_{fuel}(t)dt}{N_{fuel}}$$

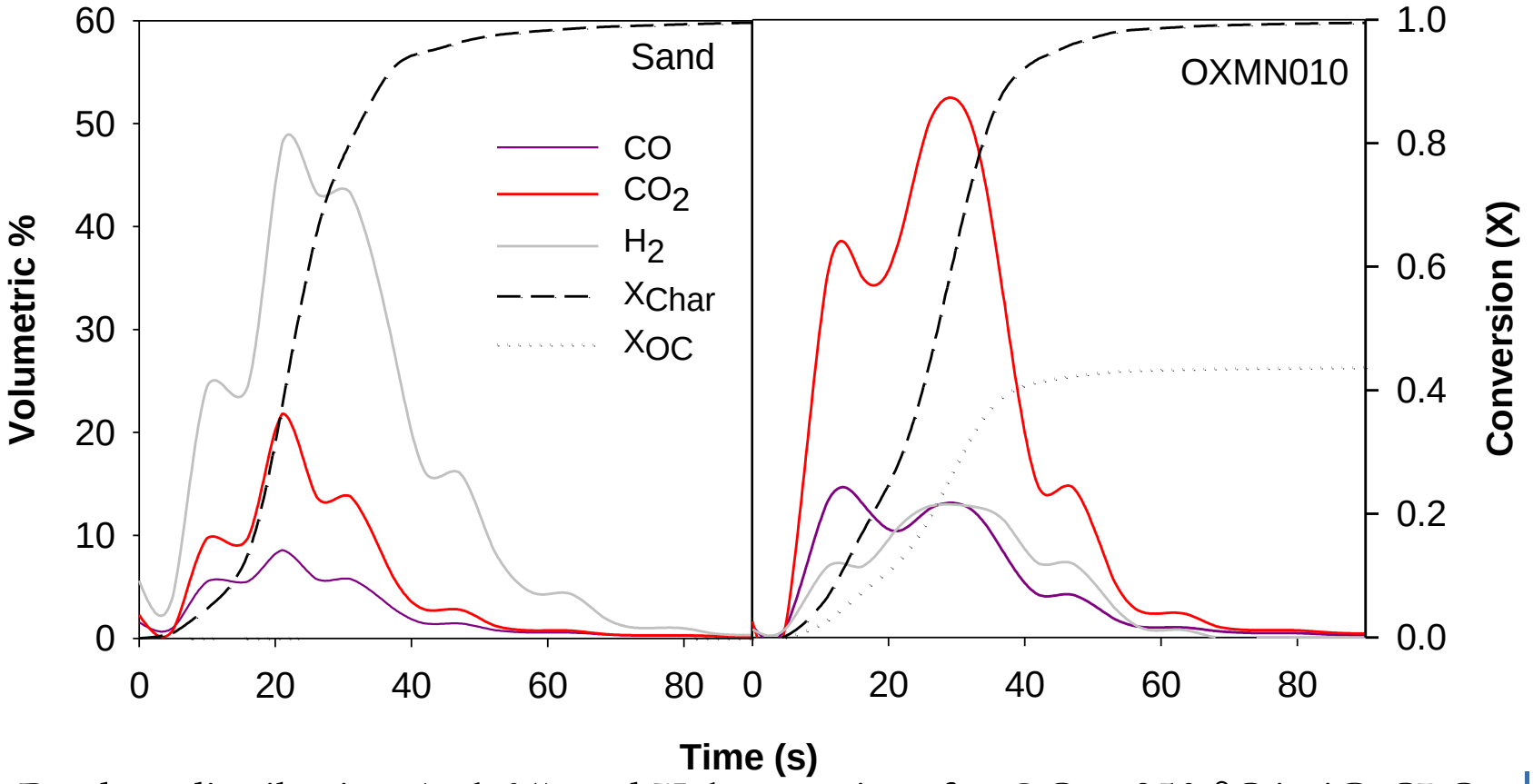
X_{fuel} = **CO 92,0 %** , **H_2 99,3 %** , CH_4 62,5 %,

Experiments in bFB with coal (*i*G-CLC)



Outlet gas stream concentration at 950 °C

Evaluation of char (X_{char}) and carrier (X_{OC}) conversion



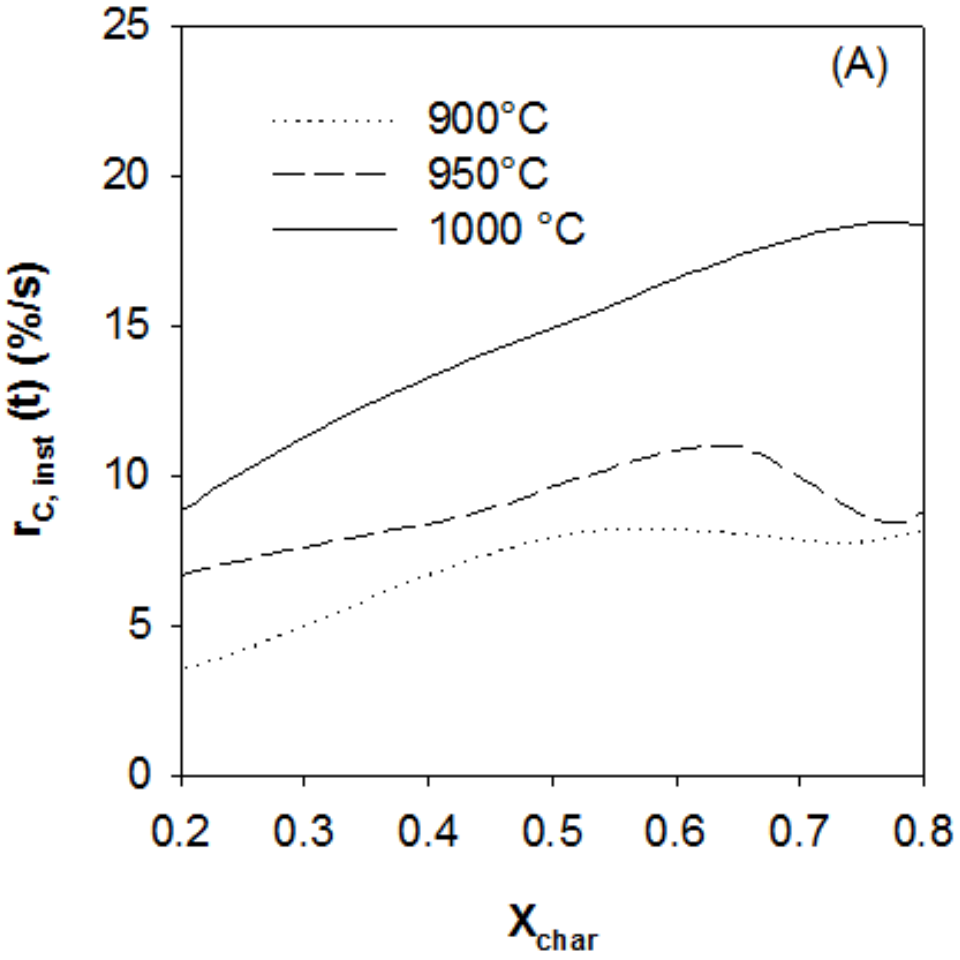
Product distribution (vol. %) and Xchar vs. time for OC at 950 °C in iG-CLC

$$X_{char}(t) = \frac{\int_0^t r_c(t)dt}{N_{C,char}}$$

$$X_{OC}(t) = \frac{1}{N_{O,OC}} \int_0^t r_O(t)dt$$

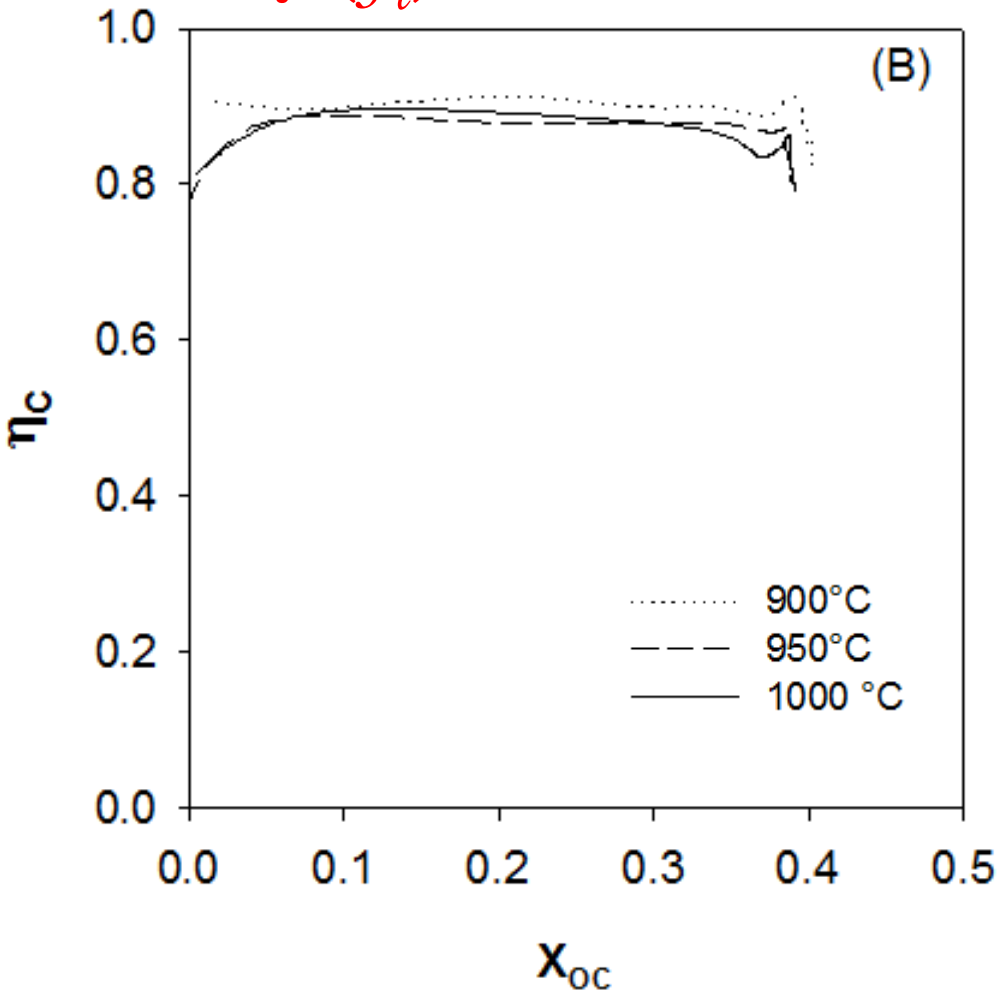
RESULTS

The influence of temperature and char conversion on the instantaneous rate of char conversion ($r_{c,inst}$).



$$r_{C,inst}(t) = \frac{r_C(t)}{N_{C,char}(1 - X_{char})}$$

The influence of OC conversion on the combustion efficiency (η_c)

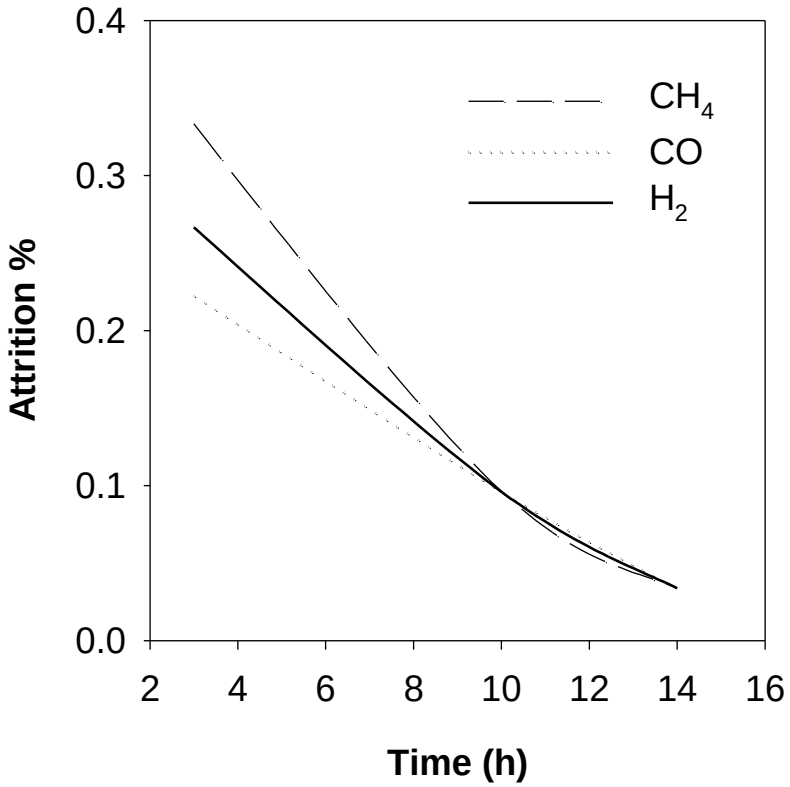


$$\eta_C(t) = \frac{r_O(t)}{2r_C(t)}$$

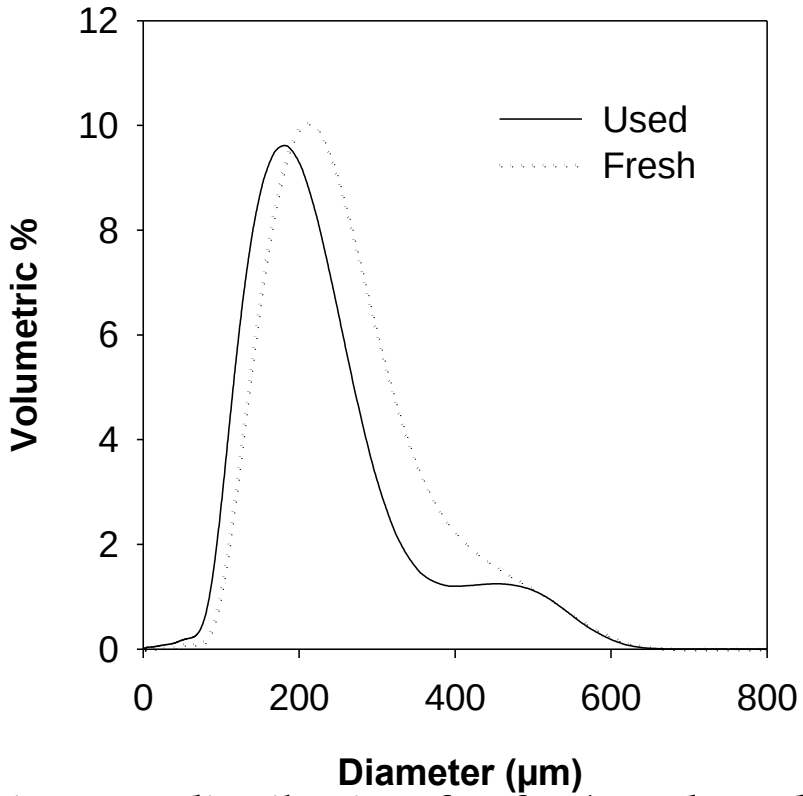
RESULTS

Evaluation of the mechanical behaviour before and after the experimentation in bFB for oxmn010 100-300

$$A = \frac{p_f}{p_t * \Delta t} * 3600 * 100$$



Effect of the fuel on the attrition rate (%/h)



Diameter distribution for fresh and used samples of OXMN010

RESULTS

EVALUATION OF THE MECHANICAL BEHAVIOUR BEFORE AND AFTER THE EXPERIMENTATION IN bFB FOR OXMN010 100-300

Parameter	Fresh	Used
AJI (%)	4,1	4,3
Crushing Strength (N)	3,0	2,0
Fe (% w/w)[a]	2,4	3,4
Mn (% w/w)[a]	38,4	36,9
Si (% w/w)[a]	15,8	17,0

CONCLUSIONS

- The conversions of OC with the gases: CO (26 % to 24 %) and H_2 (20,0%) are higher than with CH_4 (15,0%)
- Fuel conversions are better for CO (92%) and H_2 (99,3%) than with CH_4 (62,5%).
- The mineral has a good oxygen transport capacity (3,4 %), is reactive.
- The OC conversion in the *i*G-CLC process is 0,44 to 0,48 for the experiments.
- Since the mineral shows good behaviour with the products of the gasification and does not show CLOU properties, it exhibits a great potential to be used in iG-CLC.
- The mineral exhibits good mechanical and fluidization properties.

Thank you

Acknowledgements:

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