Low-cost Fe-based oxygen carrier materials for the *i*G-CLC process with coal. Part II.

Supporting Information

A. Abad, A. Cuadrat, T. Mendiara*, F. García-Labiano, P. Gayán, L. F. de Diego, J. Adánez

Department of Energy and Environment, Instituto de Carboquímica (CSIC)

Miguel Luesma Castán 4, 50018, Spain

tmendiara@icb.csic.es

Annex. Calculations.

The variation of the flow of product gas g , ($F \cdot y_g$), in a differential mass element of oxygen carrier, m_{OC} , depends on the extent of char gasification and the oxidation by the oxygen carrier, and is formulated as the rate of generation of g minus the rate of disappearance of g by its reaction with the oxygen carrier:

$$\frac{d(F \cdot y_g)}{dm_{OC}} = 2 \frac{C_C}{M_C} k_C (1 - y_g) - (1 - C_C) k_{OC} y_g \quad (i)$$

The left term in Eq. (i) can be also expressed as:

$$\frac{d(F \cdot y_g)}{dm_{OC}} = F \frac{dy_g}{dm_{OC}} + y_g \frac{dF}{dm_{OC}} \quad (ii)$$

Assuming a molar ratio between the gasifying agent and the carbon in char (G/C) equal to one:

for every mole of gasifying agent that reacts with char, there is an increase of one new mole in the total flow. Thus,

$$\frac{dF}{dm_{OC}} = \frac{C_C}{M_C} \cdot k_C (1 - y_g) \quad (\text{iii})$$

To calculate F , the total gas flow in the reactor exit, Eq. (iv) should be used, being F_0 the total gas flow at the bottom of the fuel reactor, which is the introduced gasification flow.

$$F = F_0 + \int_0^{m_{OC}} \left(\frac{dF}{dm_{OC}} \right) dm_{OC} \quad (\text{iv})$$

After replacing and operating with Eq. (i), (ii), (iii) and (iv), a complex expression is obtained, see Eq. (v), which can be only solved by numerical integration using an iterative method.

$$\int_0^{y_g} \frac{dy_g}{2 \frac{C_C \cdot k_C}{M_C} - \left[3 \frac{C_C \cdot k_C}{M_C} + (1 - C_C) \cdot k_{OC} \right] \cdot y_g + \frac{C_C \cdot k_C}{M_C} \cdot y_g^2} = \int_0^{m_{OC}} \frac{dm_{OC}}{F_0 + \int_0^{m_{OC}} \frac{C_C \cdot k_C}{M_C} (1 - y_g) \cdot dm_{OC}} \quad (\text{v})$$

In order to simplify Eq. (v), a further assumption could be made, i.e. the gas flow increases linearly with the bed mass, according to Eq. (vi):

$$F = F_o + F_{C,g} \frac{m_{OC}}{m_{OC,tot}} \quad (vi)$$

where $m_{OC,tot}$ is the total mass inventory in the fuel reactor, which is formed by the oxygen carrier and the char and $F_{C,g}$ is the flow of gasified char. With this assumption, Eq. (v) can be solved analytically. An expression to calculate the bed mass as a function of the syngas fraction is obtained, as general solution of the partial differential equation, see Eq. (vii)

$$m_{OC} = F_o \frac{m_{OC,tot}}{F_{C,g}} \left(e^{\frac{N}{D} \ln \left(\frac{y_g - a}{-a} \right) + \frac{N}{D} \ln \left(\frac{y_g - b}{-b} \right)} - 1 \right) \quad (vii)$$

where the values of D, B, a, b and N are defined as:

$$D = \frac{C_c \cdot k_c}{M_c} \cdot \frac{m_{OC,tot}}{F_{C,g}}$$

$$B = 3 + \frac{1 - C_c}{C_c} \cdot \frac{M_c \cdot k_{OC}}{k_c}$$

$$a = \frac{-B + \sqrt{B^2 - 8}}{2}$$

$$b = \frac{-B - \sqrt{B^2 - 8}}{2}$$

$$N = \frac{1}{b - a}$$

Table S1. Characterization of the Fe-based oxygen carriers used in this work

	Ilmenite	Bauxite waste	Mineral (Hematite)	Fe-Synthetic
Me_xO_y (% wt)	54.7 (Fe_2TiO_5)	71 ^a	72 ^a	15.2 ^a
	11.2 (Fe_2O_3)			
XRD main phases	Fe_2TiO_5 ,	Fe_2O_3 ,	Fe_2O_3 , SiO_2 ,	$\alpha\text{-Al}_2\text{O}_3$,
	Fe_2O_3 , TiO_2	$\beta\text{-Al}_2\text{O}_3$	CaO , MgO	Fe_2O_3
Crushing strength (N)	2.2	2.8	4.6	1.5
Oxygen transport capacity, R_{OC} , (%)	4	2.4	2.4	1.5
Porosity (%)	1.2	3.7	25.4	50.5
Skeletal density (kg/m^3)	4100	4500	4479	3950
Specific surface area, BET (m^2/g)	0.8	0.1	1	39.1

^a Determined by TGA

Table S2. Fractions in the reactor outlet of syngas (CO+H₂) and carbonaceous gases (CO+CO₂) measured in all the experiments performed with bauxite waste and all the fuels (L:lignite; MBV: South African bituminous coal; A: Anthracite), together with constants obtained with the basic model for the gasification step k_C and for the reduction reaction k_{OC} .

<i>Bauxite waste</i>									
Gasification agent: H ₂ O					Gasification agent: CO ₂				
	T(°C)	CO+H ₂ (vol.%)	CO+CO ₂ (vol.%)	k_C (s ⁻¹)	k_{OC} (mol/kg·s)	CO (vol.%)	CO+CO ₂ (vol.%)	k_C (s ⁻¹)	k_{OC} (mol/kg·s)
L	900	0.44	12.58	$5.2 \cdot 10^{-3}$	$8.42 \cdot 10^{-1}$	2.93	10.52	$3.5 \cdot 10^{-3}$	$9.6 \cdot 10^{-2}$
	950	0.73	20.00	$9.0 \cdot 10^{-3}$	$8.8 \cdot 10^{-1}$	5.80	21.70	$7.4 \cdot 10^{-3}$	$1.1 \cdot 10^{-1}$
	980	1.23	31.34	$1.5 \cdot 10^{-2}$	$9.4 \cdot 10^{-1}$	7.73	28.46	$1.0 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
MBV	900	0.15	4.78	$1.0 \cdot 10^{-3}$	$8.4 \cdot 10^{-1}$	0.52	2.07	$3.1 \cdot 10^{-4}$	$1.0 \cdot 10^{-1}$
	950	0.36	11.29	$2.0 \cdot 10^{-3}$	$8.7 \cdot 10^{-1}$	0.59	3.00	$6.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-1}$
	980	0.54	16.89	$3.0 \cdot 10^{-3}$	$9.3 \cdot 10^{-1}$	0.67	3.62	$7.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-1}$
A	900	0.07	2.52	$1.0 \cdot 10^{-3}$	$8.4 \cdot 10^{-1}$	0.16	0.57	$1.5 \cdot 10^{-4}$	$8.5 \cdot 10^{-2}$
	950	0.17	6.06	$2.0 \cdot 10^{-3}$	$8.9 \cdot 10^{-1}$	0.23	0.96	$2.2 \cdot 10^{-4}$	$1.0 \cdot 10^{-1}$
	980	0.23	8.49	$3.0 \cdot 10^{-3}$	$9.5 \cdot 10^{-1}$	0.39	2.17	$4.1 \cdot 10^{-4}$	$1.3 \cdot 10^{-1}$

Table S3. Fractions in the reactor outlet of syngas (CO+H₂) and carbonaceous gases (CO+CO₂) measured in all the experiments performed with char from South African coal (MVB) and different oxygen carriers (ILM: Ilmenite; MIN: mineral based on hematite; SYN: synthetic material), together with constants obtained with the basic model for the gasification step k_C and for the reduction reaction k_{OC} .

<i>MV Bituminous Coal</i>									
Gasification agent: H ₂ O					Gasification agent: CO ₂				
	T(°C)	CO+H ₂ (vol.%)	CO+CO ₂ (vol.%)	k_C (s ⁻¹)	k_{OC} (mol/kg·s)	CO (vol.%)	CO+CO ₂ (vol.%)	k_C (s ⁻¹)	k_{OC} (mol/kg·s)
ILM	900	0.62	5.04	$1.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-1}$	0.70	0.87	$3.6 \cdot 10^{-4}$	$1.4 \cdot 10^{-2}$
	950	0.32	3.82	$2.4 \cdot 10^{-3}$	$1.5 \cdot 10^{-1}$	0.90	1.31	$5.5 \cdot 10^{-4}$	$1.7 \cdot 10^{-2}$
	1000	0.75	9.54	$3.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-1}$	1.12	1.75	$7.4 \cdot 10^{-4}$	$1.8 \cdot 10^{-2}$
MIN	900	1.05	2.64	$8.9 \cdot 10^{-4}$	1.4	0.86	1.45	$3.1 \cdot 10^{-4}$	$9.3 \cdot 10^{-1}$
	950	1.19	3.19	$1.2 \cdot 10^{-3}$	1.4				
	980	1.97	5.36	$1.7 \cdot 10^{-3}$	1.5	2.18	3.90	$7.1 \cdot 10^{-4}$	$9.8 \cdot 10^{-1}$
SYN	900	0.67	2.52	$6.6 \cdot 10^{-4}$	2.8	0.71	1.50	$3.0 \cdot 10^{-4}$	1.5
	980	1.12	4.62	$1.4 \cdot 10^{-3}$	3.2	2.83	6.61	$9.3 \cdot 10^{-4}$	1.7