Methane Combustion in a 500 W_{th} Chemical-Looping Combustion System Using an Impregnated Ni-based Oxygen Carrier

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ABSTRACT. Chemical-looping combustion (CLC) is a promising method for the combustion of fuel gas with CO₂ capture and sequestration (CCS). This paper presents the methane combustion results obtained in a continuous CLC prototype using an oxygen carrier containing 18 wt% NiO impregnated on alumina. The design of the CLC prototype was a circulating fluidized bed reactor, consisting of two interconnected fluidized bed reactors, the fuel reactor (FR) and the air reactor (AR). The main operating conditions affecting combustion, as fuel gas flow, solids circulation rate, and FR temperature, were analyzed. The CLC operation was carried out using methane as fuel gas in the FR with a thermal power between 500 and 850 W_{th}. The prototype was successfully operated during 100 h, of which 70 h were at

combustion conditions. No methane was detected at the FR exit, being CO and H₂ the unconverted gases. Increasing the temperature in the FR or the solids circulation rates increased the combustion efficiency, reaching efficiencies values as high as 99% at temperatures in the range 1073-1153 K, and a solid inventory in the FR of 600 kg per MW_{th}. The effect of operating conditions on the performance of the oxygen carrier in the CLC prototype was analyzed. During operation of the CLC prototype, no signs of agglomeration or carbon formation were detected and the main properties of particles did not vary. The two different phases in the oxygen carrier, NiO and NiAl₂O₄, were active to transfer oxygen to the fuel gas. The NiO/NiAl₂O₄ ratio increased with a decrease in the solids circulation rate, which affected to the reactivity of the oxygen carrier.

INTRODUCTION.

Anthropogenic greenhouse gas emissions highly contribute to the global warming problem. According to the Intergovernmental Panel on Climate Change (IPCC), carbon dioxide is the most important anthropogenic greenhouse gas.¹ The global atmospheric concentration of CO₂ has increased from a pre-industrial value of about 280 ppm to 379 ppm in 2005. The main contributor to this increase is fossil fuel use and about a third of the global CO₂ emissions come from their burning in power plants.

It is necessary therefore to enlarge the efforts to mitigate this impact as much as possible. Among the different opportunities to reduce the anthropogenic CO₂ emissions, the possibility to capture and store CO₂ (CCS) has been identified as a relevant option in the future. Using available technologies, the most important economic and energetic cost for CCS is related to the CO₂ capture process.² Capture of CO₂ means to separate CO₂ from the processes where the fossil fuels are being used to obtain a CO₂-rich stream ready to be stored. In this sense, Chemical-Looping Combustion (CLC) has been suggested as one of the most promising technologies for reducing the costs of CO₂ capture using fossil fuels.^{2,3}

CLC is a two-step combustion process that produces a pure CO₂ stream, ready for compression and sequestration. Research in CLC process is an active area and has been widely analyzed by the literature for combustion of natural gas⁴⁻¹¹ or for gas from coal gasification.^{5,12-14} Recently, interest has arisen about combustion of solid fuels, e.g. coal, introducing the fuel directly to the system where the

gasification of the solid fuel and subsequent reactions of gasification gases with the oxygen carrier particles will occur simultaneously in the same reactor.¹⁵⁻¹⁸

The most common design of a CLC plant includes a high-velocity riser for the air reactor (AR) and a low-velocity fluidized bed for the fuel reactor (FR), with the oxygen carrier in the form of metal oxide particles circulating between them. In the FR, the metal oxide is reduced by the following general reaction for methane:

where Me_xO_y denotes a metal oxide and $\text{Me}_x\text{O}_{y-1}$ its reduced compound.

The particles of the oxygen carrier are transported to the AR where they are regenerated by taking up oxygen from the air:

The oxidized carrier is returned to the FR for a new cycle. In this system, the solid oxygen carrier is used to transport oxygen from the combustion air to the fuel. Since the fuel is not mixed with air, the subsequent CO_2 separation process is not necessary. The total amount of heat evolved from reactions 1 and 2 in the two reactors is the same as for normal combustion, where the oxygen is in direct contact with fuel.

Preliminary designs of full-scale CLC systems have been proposed to be similar to a circulating fluidized bed (CFB)⁷ and the CLC technology has been successfully demonstrated for methane or natural gas combustion in different prototypes of interconnected fluidized beds. A 50 kW_{th} unit at the Korea Institute of Energy Research was operated during 3.5 h with methane as fuel and oxygen carriers based on nickel and cobalt oxide.¹⁹ Longer operation times were successfully conducted in two different 10 kW_{th} prototypes built at Chalmers University of Technology (CUT)²⁰⁻²¹ and the Instituto de Carboquímica (ICB-CSIC).²² The first one was operated using NiO-based oxygen carriers prepared by freeze granulation (105 h) and spin flash drying (160 h) methods. The later one was run during 200 h using a CuO-based oxygen carrier prepared by impregnation method. Because of the efforts and costs associated with these systems, e.g. the large amount of oxygen carrier needed, smaller units have been

designed and operated, where different types of oxygen carriers can be tested in a way which closely simulates conditions of CLC system. A 300 W_{th} laboratory reactor system was used for natural gas combustion using NiO/MgAl₂O₄, NiO/NiAl₂O₄, Mn₃O₄/Mg-ZrO₂ and Fe₂O₃/Al₂O₃ oxygen carriers prepared by freeze granulation.²³⁻²⁶ This reactor consists in two-compartment fluidized bed, which were interconnected to permit solids circulation between both reactors. A different design was used by Son and Kim: an annular shape circulating fluidized bed reactor with double loops was operated for CH₄ combustion ranging from 300 to 1500 W_{th}.²⁷ NiO- and Fe₂O₃-based oxygen carriers supported on bentonite was tested in this unit.

The selection of the oxygen carrier is a key factor for the CLC technology development. In general, the oxygen carrier is based on a transition state metal oxide, e.g. CuO, NiO, CoO, Fe₂O₃ or Mn₃O₄, which is supported on different inert material, as Al₂O₃, SiO₂, TiO₂ or yttrium stabilized zirconia (YSZ). An oxygen carrier in a CLC power plant must show high reaction rates and oxygen transference capacity, complete fuel conversion to CO₂ and H₂O; negligible carbon deposition, avoidance of agglomeration, and sufficient durability as well as good chemical performance in successive cycle reactions. In addition, the cost of the oxygen-carrier, environmental characteristics and health aspects are also important. Among the different metal oxides proposed, Ni-based oxygen carriers have shown very high reactivity, and allow working at high temperatures (1200-1400 K) in a CLC process with full CH₄ conversion, although thermodynamic restrictions result in a small presence of CO and H₂ in the gas outlet of the FR.²⁸ Nickel is more expensive than other metal oxides, although this problem may be solved using particles with low nickel content, high reactivity, and low attrition rate.¹¹ Moreover, the use of Ni-based oxygen carriers may require safety measures because of its toxicity.

NiO-based oxygen carriers have been extensively analyzed in the literature. Pure NiO particles has low reaction rate due to their low porosity.²⁹ In order to increase the reactivity and regenerability of the oxygen carrier particles, a number of NiO-based solid particles fashioned by different preparation methods and using different compounds as support material have been tested. A selected group of oxygen carriers seems to be very promising to be used in a CLC system because their high reactivity

1 during reduction and oxidation reactions, regeneration capacity for repeated redox cycles, and
2 durability. Table 1 summarizes a review of most NiO-based particles investigated and the testing
3 conditions to evaluate their feasibility as oxygen carrier for a CLC system. The use of Al₂O₃-based
4 compounds as support material has been extensively investigated in the literature. In general, reduction
5 of NiO/Al₂O₃ particles was limited by the partial transformation of NiO into NiAl₂O₄ spinel
6 compound,^{6,27,29,30} which has poor reactivity for CLC.³¹ Nevertheless, high reactivity and low NiAl₂O₄
7 formation was found in some cases using mechanical mixing or impregnation methods.³²⁻³⁶ However,
8 particles prepared by mechanical mixing were rejected due to their low crushing strength.^{27,33} Ni-based
9 oxygen carriers prepared by impregnation on α -Al₂O₃ showed very high reactivity, showing low
10 attrition rates and agglomeration avoidance problems during operation in fluidized beds.³⁴ To avoid the
11 interaction between metal and support to form NiAl₂O₄, different alumina-based compounds have been
12 proposed as support material. Excellent reactivity and regenerability was found for particles using
13 NiAl₂O₄, MgAl₂O₄, CaAl₂O₄ and LaAl₁₁O₁₆ as support material because the lower interaction between
14 NiO and support.^{11,28,29,31,34,37-43} In most cases, oxygen carriers supported on Al₂O₃ compounds showed
15 very high reactivity with methane compared to others metal oxides,^{11,27,29,32,33,42,44,45}, no agglomeration
16 problems and low attrition rates during operation in fluidized beds,^{20,21,23,24,34,46,47} and avoidance of
17 carbon deposition at CLC conditions.^{20,21,23,24,34,48,49} Differences on the behaviour of NiAl₂O₄ and
18 MgAl₂O₄ as inert material were investigated by Villa et al.³¹ Oxygen carrier prepared by Ni–Al–O
19 mixtures consisted of cubic NiO and NiAl₂O₄ spinel. They found that Mg addition to NiO/NiAl₂O₄
20 particles improves regenerability upon repeated redox cycles. Erri and Varma found similar results.³⁵
21 Addition of Mg to the NiO/Al₂O₃ mixture improved the stability of the spinel structure of the support
22 material, i.e. MgAl₂O₄ in this case.

23 In general, the use of others compounds as support material have shown problems on reactivity,
24 mechanical strength, defluidization or carbon formation. Particles using zirconia (ZrO₂)^{28,33} or YSZ²⁹ as
25 inert material presented good reactivity, but mechanical strength values were low or particles broke due
26 to cracks formed on the surface layer of the particle after five redox cycles. Lower reactivity was shown

1 using bentonite,²⁷ specially at temperatures above 1073 K⁵⁰ or 1173 K.⁵¹⁻⁵³ Very slow or not reaction
2 was found for TiO₂ and MgO support material because the formation of stable complex compounds,
3 NiTiO₃ and Mg_{0.4}Ni_{0.6}O respectively,^{27-30,54} except for those prepared by mechanical mixing that were
4 calcined at temperatures in the range 1373-1473 K.³³ Also low reactivity, deactivation as a function of
5 the cycle or low mechanical strength was seen for NiO supported on SiO₂^{33,42} or sepiolite.³³

6 Among the different methods of preparation of oxygen carrier particles, impregnation is an easy
7 method, available for industrial applications, which could reduce the particle production costs. In a
8 previous work it was found that NiO-based solid prepared by impregnation on α -Al₂O₃ was a promising
9 oxygen carrier for CLC application.³⁴ From discontinuous tests carried out in TGA and batch fluidized
10 bed, high oxygen transference rates were obtained using a relatively low NiO content in the solid
11 material (11-38 wt%). However, limited information can be obtained from discontinuous experiments.
12 In order to gain a more adequate understanding of the behavior and usefulness of the particles in this
13 process, tests are needed in a real system where the particles are continuously circulated between an air
14 and a fuel reactor. The objective of this work was to test the suitability of this NiO-based oxygen carrier
15 for methane combustion in a continuously operated CLC system. For this purpose, a 500 W_{th} chemical-
16 looping combustor was used. The effect of operating conditions, such as the oxygen carrier to fuel ratio
17 and the FR temperature, on the combustion efficiency has been determined. Moreover, the evolution of
18 the oxygen carrier properties and its behavior during the operation test was analyzed. Special attention
19 was paid in the NiAl₂O₄ spinel phase development.

2 **Table 1.** Literature data on NiO-based oxygen carriers.

Support material	NiO fraction (wt%)	Preparation method ^a	Facility ^b	Reacting gas ^c	Reference
none	100	MM+SD	TGA	CH ₄ , H ₂ , O ₂	[29]
Al ₂ O ₃	60	MM or DIS+SD	TGA	CH ₄ , CO, H ₂ , O ₂	[29,30]
Al ₂ O ₃	40-80	MM+EXT	TGA	CH ₄ , O ₂	[33]
Al ₂ O ₃	60	MM+C&S	TGA	CH ₄ , O ₂	[27]
Al ₂ O ₃	--	IMP	TGA	CH ₄	[6]
Al ₂ O ₃	33	IMP	TGA	CH ₄ , O ₂	[32]
Al ₂ O ₃	11-38	IMP	TGA, FB	CH ₄ , O ₂	[34]
Al ₂ O ₃	5-20	IMP	TPR, FB	CH ₄	[35,36]
NiAl ₂ O ₄	14-60	COP	TPR	CH ₄ , H ₂ , O ₂	[31]
NiAl ₂ O ₄	20-40	SC+MM+C&S	TGA	CH ₄ , syngas	[37]
NiAl ₂ O ₄	60	DIS+SD	TGA	H ₂	[29]
			CLC	H ₂	[55]
NiAl ₂ O ₄	60	DIS+EXT	PB	CH ₄	[38]
NiAl ₂ O ₄	60-90	DIS+C&S	FB	H ₂	[39]
NiAl ₂ O ₄	60	DIS+C&S	TGA	CH ₄ , H ₂ , O ₂	[40]
NiAl ₂ O ₄	40	FG	10 kW CLC	n.g.	[20]
			FB	CH ₄ , O ₂	[28,44,46,48]
			TGA	CH ₄ , CO, H ₂ , O ₂	[11]
NiAl ₂ O ₄	60	FG	300 W CLC	n.g.	[24]
			FB	CH ₄ , O ₂	[45,47,49]
NiAl ₂ O ₄	60	SF	10 kW CLC	n.g.	[21]
MgAl ₂ O ₄	35	COP	TPR	CH ₄ , H ₂ , O ₂	[31]
MgAl ₂ O ₄	30	SC+MM+C&S	TGA	CH ₄ , syngas	[37]
MgAl ₂ O ₄	60	FG	300 W CLC	n.g., syngas	[23,24]
			FB	CH ₄ , O ₂	[28,44,48]
			TGA	CH ₄ , O ₂	[41]
MgAl ₂ O ₄	35	FG+IMP	TGA	CH ₄ , O ₂	[42]
MgAl ₂ O ₄	20	MM+IMP or IMP	TGA, FB	CH ₄ , O ₂	[34]
CaAl ₂ O ₄	40	FG	FB	CH ₄ , O ₂	[28,44]
CaAl ₂ O ₄	20	MM+IMP or IMP	TGA, FB	CH ₄ , O ₂	[34]
LaAl ₁₁ O ₁₈	20-40	IMP	TGA	H ₂ , O ₂	[43]
ZrO ₂	40-80	MM+EXT	TGA	CH ₄ , O ₂	[33]

ZrO ₂	40	FG	FB	CH ₄ , O ₂	[28]
YSZ	60	MM/SG/DIS + SD	TGA	CH ₄ , H ₂ , O ₂	[29]
YSZ	20-80	DIS+MM+SD	TGA	H ₂ , CO	[30]
Bentonite	60	MM+C&S	TGA, 1.5 kW CLC	CH ₄ , O ₂	[27]
Bentonite	26-78	MM+C&S	TGA	CH ₄ , O ₂	[50]
Bentonite	60	MM+C&S	50 kW CLC	CH ₄	[19]
			TGA, PB	CH ₄ , O ₂	[51,52]
Bentonite	60	MM+C&S	TGA, TEOM, PB	syngas	[53]
TiO ₂	60	MM+C&S	TGA	CH ₄ , O ₂	[27]
TiO ₂	40-80	MM+EXT	TGA	CH ₄ , O ₂	[33]
TiO ₂	60	MM+SD	TGA	CH ₄ , H ₂ , CO, O ₂	[29,30]
TiO ₂	40-80	FG	FB	CH ₄ , O ₂	[28]
TiO ₂	34-44	IMP	PB	CH ₄	[54]
MgO	60	DIS+SD	TGA	CH ₄ , H ₂ , O ₂	[29]
MgO	60	FG	FB	CH ₄ , O ₂	[44]
SiO ₂	40-80	MM+EXT	TGA	CH ₄ , O ₂	[33]
SiO ₂	35	IMP	TGA	CH ₄ , O ₂	[42]
Sepiolite	40-80	MM+EXT	TGA	CH ₄ , O ₂	[33]

^a Key for preparation method:

C&S: crush and sieve
COP: coprecipitation
DIS: dissolution
EXT: extrusion
FG: freeze granulation
IMP: impregnation
MM: mechanical mixing
SC: solution combustion
SD: spray drying
SF: spin flash
SG: sol-gel

^b Key for facility:

CLC: continuously operated CLC system
FB: fluidized bed
PB: packed bed
TGA: thermogravimetric analyzer
TEOM: tapered element oscillating microbalance
TPR: temperature programmed reduction

^c Key for reacting gas:

n.g.: natural gas

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EXPERIMENTAL SECTION.

A Ni-based oxygen carrier prepared by hot incipient wet impregnation (HIWI) at ICB-CSIC has been used in the 500 W_{th} CLC prototype. The CLC prototype has been running for 100 hours with solid particles circulation at hot conditions, of which 70 h were with combustion using CH₄ as fuel gas and 30 h fluidizing using N₂ during stabilization periods.

Oxygen carrier. A Ni-based oxygen carrier prepared by HIWI method on α -Al₂O₃ was used in the tests. The support material (α -Al₂O₃) was obtained from calcination of commercial γ -Al₂O₃ (Puralox N_{Wa}-155, Sasol Germany GmbH) during 2 hours at 1423 K. The resulting particles had a density of 2000 kg/m³ and a porosity of 0.47. The HIWI method consist of the addition to α -Al₂O₃ particles of a volume of a saturated solution (6 M) of Ni(NO₃)₂·6H₂O (>99.5% Panreac) at 353 K corresponding to the total pore volume of particles. Two consecutives impregnation steps were carried out to obtain the desired NiO concentration into particles (18 wt%). The resulting powder was calcined at 823 K in air atmosphere for 30 min, to decompose the impregnated metal nitrate into insoluble metal oxide. Finally, the oxygen carrier particles were sintered for 1 h at 1223 K.

The main characteristics of the material –denoted here as Ni18- α Al:HI– are showed in Table 2. The oxygen transport capacity was defined as the mass fraction of oxygen that can be used in the oxygen transfer, calculated as $R_{OC} = (m_{ox} - m_{red})/m_{ox}$, where m_{ox} and m_{red} are the masses of the oxidized and reduced form of the oxygen carrier, respectively.

Characterization of Oxygen Carriers. Both fresh oxygen carrier particles, i.e. particles not subjected to CLC operation, and particles used in the 500 W_{th} CLC prototype, were physically and chemically characterized by several techniques. Particle porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33, solid density was measured by He Micromeritics AccuPyc II 1340 picnometer, and specific surface area was determined by N₂ physisorption using a Micromeritics ASAP-2020 apparatus. The particle size distribution was obtained using a Beckman Coulter LS13320 apparatus. The force needed to fracture a particle was determined using a Shimpo FGN-5X crushing

strength apparatus. The crushing strength value was taken as the average value of at least 20 measurements.

Table 2. Properties of the oxygen carrier Ni18- α Al:HI as prepared (fresh) and used for 100 h in the CLC prototype.

	Fresh	Used
NiO content, w_0 (wt %)	18	18
Oxygen transport capacity, R_{OC}	0.0386	0.0386
Particle size (mm)	0.1-0.3	0.1-0.3
Porosity	0.40 $\pm$ 0.01	0.42 $\pm$ 0.01
Solid density (kg m ⁻³)	4290 $\pm$ 20	4250 $\pm$ 20
Particle density (kg m ⁻³)	2470 $\pm$ 10	2480 $\pm$ 10
Specific surface area BET (m ² g ⁻¹)	7.0 $\pm$ 0.2	6.8 $\pm$ 0.2
Crushing strength (N)	4.1 $\pm$ 0.3	3.7 $\pm$ 0.2

The microstructures of the particles and element distribution in the solid were observed by scanning electron microscope (SEM) on a Hitachi S-3400N microscope equipped with a Routec XFlash EDX analyzer. The identification of crystalline chemical species was carried out by powder X-ray diffraction (XRD) patterns acquired in an X-ray diffractometer Bruker AXS D8ADVANCE using Ni-filtered Cu-K α radiation equipped with a graphite monochromator. To elucidate chemical species between NiO or NiAl₂O₄ and to determine the fractional amount of each one, temperature programmed reduction (TPR) were performed using H₂ as reducing agent in an AutoChem II Micromeritics equipment and in a CI Electronics Ltd type thermogravimetric analyzer (TGA) described elsewhere.³³ Eventually, reactivity tests were performed in the above mentioned TGA using CH₄ as fuel gas for reduction and air for oxidation.

1 setting the solids ready to be fed to the FR. Leakage of gas between both reactors was prevented by the
2 presence of the U-shaped loop seal (2) and the solids reservoir (7). The regenerated oxygen carrier
3 returned to the FR by gravity through a solids valve (8) which controlled the flow rates of solids
4 entering the FR. A diverting solids valve (6) located below the cyclone allowed the measurement of the
5 solids flow rates at any time. So, this design allowed to control and to measure the solids circulation
6 flow rate between both reactors. The fines produced by fragmentation/attrition in the plant were
7 recovered in filters (9) located downstream of the AR and FR. Because of the compact size of the
8 system, this facility can be used to test several promising oxygen carriers using smaller amounts of
9 solids than in larger facilities. Typically, the total solids inventory in the system was in the range 0.8-1.5
10 kg depending on the density of particles.

11 Different samples of used particles in the 500 W_{th} CLC prototype were taken during CLC operation in
12 order to characterize their properties depending on the experimental conditions, mainly among the
13 solids circulation rate. By the one hand, fully oxidized particles were taken during solid circulation
14 measurement at the cyclone outlet. By the other hand, partially reduced samples were taken from the FR
15 after the end of a working day. In this case, solids circulation was stopped sending the solids to a
16 deposit after cyclone separation by the use of the diverting solids valve (6) and closing the solids valve
17 (8). At same time, CH₄ flow was replaced by nitrogen to avoid any change in solids conversion after
18 operation was stopped. Finally, a sample of solids was extracted from the FR after reactor cooling.

19 The prototype was provided with several tools of measurement and system control. Thermocouples
20 and pressure transducers located at different points of the plant showed the current operating conditions
21 in the plant at any time. The AR and FR temperatures were controlled separately. Accurate flow rates of
22 feeding gases were obtained by means of specific mass flow controllers. The gas outlet streams of the
23 AR and FR were drawn to respective on-line gas analyzers to get continuous data of the gas
24 composition. The outlet gas from the FR was composed by N₂, CO₂, H₂O, and unburnt CO and H₂. The
25 composition of gases from the AR was N₂ and unreacted O₂. If carbon formation on particles occurs in
26 the FR, also CO and CO₂ could appear in the AR because of its combustion by air. CH₄, CO, H₂, and

CO₂ concentrations were measured at the gas outlet stream from the FR after steam condensation, whereas O₂, CO, and CO₂ concentrations were measured at the gas outlet stream from the AR. Nondispersive infrared (NDIR) analysers (Maihak S710/UNOR) were used for CO, CO₂, and CH₄ concentrations determination, a paramagnetic analyser (Maihak S710/OXOR-P) for O₂ concentration, and a thermal conductivity detector (Maihak S710/THERMOR) for H₂ concentration. All data was collected by means of a data logger connected to a computer.

Testing conditions. Combustion tests under different operation conditions were conducted in the facility with the Ni18- α Al:HI oxygen carrier. The total solids inventory in the system was ≈ 1.2 kg of solid material, which 0.3 kg and 0.5 kg was in the FR and AR, respectively. The oxidation of the oxygen carrier took place in the dense bed part of the AR allowing residence times high enough for achieving the complete oxidation of the reduced carrier, according to eq 2. A total of about 100 hours at hot conditions, of which 70 hours corresponded to combustion conditions, were carried out using the same batch of oxygen carrier particles. The fuel gas in the FR was methane diluted in nitrogen. The inlet flow in the FR was 170 L_N/h, and no steam was added in the FR feeding gas. The inlet gas velocity in the FR was 0.1 m/s, i.e., about 3 times the minimum fluidization velocity for 0.3 mm particles. Air was used as fluidizing gas in the AR, which was divided into the fluidizing gas in the bottom bed (720 L_N/h) and the secondary air in the riser (150 L_N/h). Nitrogen was used as fluidizing agent in the particle loop-seal (37.5 L_N/h).

Two different experimental test series were carried out. Table 3 shows a compilation of the main variables used in each test. In test series A01-A18, the effect of the oxygen carrier to fuel ratio (ϕ) on the gas combustion efficiency was analyzed by controlling the solid circulation flow rates by means of the solids valve. The oxygen carrier to fuel ratio (ϕ) was defined by the following equation

$$\phi = \frac{F_{\text{NiO}}}{4F_{\text{CH}_4,0}} \quad (3)$$

where F_{NiO} is the molar flow rate of NiO and $F_{\text{CH}_4,0}$ is the inlet molar flow rate of CH₄ in the FR. A value of $\phi = 1$ corresponds to the stoichiometric NiO-CH₄ in the reaction 1. Methane concentration in

the fuel gas was set to be 30 vol% –nitrogen to balance– corresponding to 500 W_{th}. In the experimental test series B01-B13, the effect of the fuel flow on the combustion efficiency was analyzed changing the fuel concentration, but gas velocity and solids circulation rate were maintained roughly constant. Therefore, the fuel flow varied in this experimental test series. Different CH₄ concentrations ranging from 30 to 50 vol%, corresponding to power input between 500 and 850 W_{th}, were used. For both tests series, experiments were conducted at three different temperatures in the FR (1073, 1123 and 1153 K). In all cases, the temperature in the AR was kept constant at 1223 K. Air flow into the AR was maintained constant for all test, remaining always in excess over the stoichiometric oxygen demanded by the fuel gas. The air excess ratio, λ defined in eq 4, ranged from 1.07 to 1.80, depending on the fuel flow.

$$\lambda = \frac{\text{Oxygen flow}}{\text{Oxygen demanded}} = \frac{0.21F_{\text{air}}}{2F_{\text{CH}_4}} \quad (4)$$

In order to evaluate the behavior of the oxygen carriers during the combustion tests, the combustion efficiency, η_c , was used as key parameter. The combustion efficiency is defined as the ratio of the amount of oxygen consumed by the gas leaving the fuel reactor to the amount of oxygen consumed by the gas when the gas conversion is complete to CO₂ and H₂O, see eq 5. So, the η_c parameter gives how the CLC operation is close or far from the full combustion of fuel, i.e. $\eta_c = 100\%$.

$$\eta_c = \frac{2x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{H}_2\text{O}}}{4(x_{\text{CH}_4} + x_{\text{CO}_2} + x_{\text{CO}})} \quad (5)$$

where x_j is the molar fraction of the gas j in the outlet gas stream from the FR. CH₄, CO₂, CO and H₂ concentrations in the flue gas from the FR were analyzed. H₂O concentration was estimated assuming no carbon formation via the following equation

$$x_{\text{H}_2\text{O}} = 2(x_{\text{CO}_2} + x_{\text{CO}}) - x_{\text{H}_2} \quad (6)$$

Avoidance of carbon formation was evidenced during experimental work, as it is discussed below.

1

2 **Table 3.** Main data for experimental tests in the CLC prototype.

Reference	Duration (min)	T_{FR}	ϕ	Power (W_{th})	CH ₄ (vol%)	f_s (kg/h)	f_s^* (kg s ⁻¹ MW ⁻¹)	m_{FR}^* (kg/MW _{th})
A01	90	1153	0.95	500	30	3.6	2.0	600
A02	90	1153	1.13	500	30	4.3	2.4	600
A03	90	1153	1.24	500	30	4.7	2.6	600
A04	90	1153	1.37	500	30	5.2	2.9	600
A05	600	1153	1.50	500	30	5.7	3.2	600
A06	90	1153	1.64	500	30	6.2	3.5	600
A07	90	1153	1.91	500	30	7.2	4.0	600
A08	120	1153	2.06	500	30	7.8	4.4	600
A09	90	1153	2.24	500	30	8.5	4.8	600
A10	600	1153	2.74	500	30	10.4	5.8	600
A11	120	1153	3.09	500	30	11.7	6.5	600
A12	120	1123	1.53	500	30	5.8	3.2	600
A13	90	1123	1.70	500	30	6.4	3.6	600
A14	90	1123	2.42	500	30	10.8	5.1	600
A15	120	1123	3.06	500	30	11.6	6.5	600
A16	120	1073	1.95	500	30	8.7	4.1	600
A17	90	1073	2.40	500	30	9.1	5.1	600
A18	90	1073	3.06	500	30	11.6	6.5	600
B01	120	1153	2.65	500	30	10.0	5.6	600
B02	90	1153	2.15	590	35	9.6	4.5	510
B03	90	1153	1.82	680	40	9.4	3.9	440
B04	90	1153	1.56	850	50	10.1	3.3	355
B05	90	1153	1.40	850	50	9.0	3.0	355
B06	120	1123	3.09	500	30	11.7	6.5	600
B07	90	1123	2.42	590	35	10.8	5.1	510
B08	90	1123	1.92	680	40	9.9	4.1	440
B09	90	1123	1.58	850	50	10.2	3.4	355
B10	90	1073	2.40	500	30	9.1	5.1	600
B11	90	1073	1.95	590	35	8.7	4.1	510
B12	90	1073	2.19	680	40	11.3	4.6	440
B13	90	1073	1.58	850	50	10.2	3.4	355

RESULTS AND DISCUSSION

To determine the behavior of the Ni18- α Al:HI oxygen carrier during methane combustion, several tests were carried out at different temperatures, methane concentration and solids circulation rate. The CLC prototype was easy to operate and control, and the steady-state for each operating conditions was maintained at least for 90 min. As an example, evolution with time of temperature and gas concentration from the air and fuel reactors is shown in Figure 2 for experimental test A10. This experimental test was repeated several times among the experimental tests, obtaining similar results in all cases. The temperature in the FR was 1153 K and the solids circulation rate was 10.4 kg/h, corresponding to a ϕ value of 2.74. Full conversion of CH₄ was obtained in the FR, and a CO₂ concentration about 25 vol% (dry basis) was observed at the FR outlet. This value was somewhat lower than the inlet CH₄ concentration (30 vol%) as a consequence of the dilution produced by N₂ coming from the loop seal, and because some CO and H₂ are also obtained at the outlet. Using measured gas composition and eq 6 to calculate H₂O concentration, in all cases the water gas shift (WGS) equilibrium matched to lower temperatures than the FR temperature, likely because WGS equilibrium is reached downstream the FR, where the temperature is lower.

Stable combustion was reached usually in less than 10 minutes. After this startup time, the gas outlet concentration and temperature was maintained uniform during the whole combustion time. Mass balances were found to be accurate by using the measurements of the analyzers from the AR and FR. From these results it is possible to calculate the rate of oxygen reacted in the AR, $\dot{m}_{O,AR}$, and the rate of oxygen transferred from the oxygen carrier to the fuel gas in the FR, $\dot{m}_{O,FR}$. The stoichiometric index Φ_{ox} is defined as the ratio between oxygen reacted in the AR and FR⁵⁵

$$\Phi_{ox} = \frac{\dot{m}_{O,AR}}{\dot{m}_{O,FR}} \quad (7)$$

Figure 2. Temperature, Φ_{ox} factor, and gas product distribution at the outlet of AR and FR during a typical experiment. Experimental test A10: T_{FR} = 1153 K; T_{AR} = 1223 K; CH₄: 30 vol%; f_S = 10.4 kg/h; ϕ = 2.74.

A stoichiometric index lower than unity means that a fraction of the oxygen taken up in the FR comes from the oxygen initially present in the oxygen carrier, which is the case in the first period after fuel addition, see Figure 2. During the stationary combustion period the stoichiometric index was around unity, which can be considered as a good verification of the steady state operation. This means that the amount of oxygen taken from the air is equal to the amount of oxygen transferred in the FR. Similar results were found for all tests.

Carbon formation. A suitable oxygen-carrier should not promote formation of solid carbon in the FR. Carbon deposited on particles could be transported to the AR, where combustion with oxygen will happen. In this case, CO₂ will be emitted from the AR, reducing the carbon capture efficiency of the chemical-looping combustor. Using Ni-based oxygen carriers, carbon deposition on particles could happen in the FR because metallic Ni is formed during reaction of the oxygen carrier with the fuel gas, which catalyses methane decomposition and Boudouard reaction

In the CLC prototype, carbon formation was evaluated by measuring CO and CO₂ concentration in the outlet from the AR. As mentioned previously, there was not gas leakage from the FR to AR; therefore any carbon containing gas present in the AR outlet should come from solid carbon following the oxygen carrier particles. CO or CO₂ was not detected in the AR outlet stream in any test. Additional tests were performed to determine if carbon was accumulated on particles or somewhere in the system, e.g. reactor walls or distributor plate. In these tests, the fuel gas was turned off and FR was fluidized with nitrogen. After two minutes nitrogen was replaced by air as fluidization agent, so any carbon deposition in the system should burn into CO or CO₂. However, no CO or CO₂ was detected in the flue gases in any case. From these results, it was concluded that carbon formation did not happen at relevant extension in the system, i.e. deposited on the oxygen carrier particles nor anywhere in the FR.

Effect of operating conditions on combustion efficiency. To study the effect of the oxygen carrier to fuel ratio, ϕ , several experiments were done using different solids circulation rates, and maintaining constant all the other experimental conditions (series A in Table 3). The circulation rate of oxygen carrier particles, controlled by the solid valve, was varied over a range of 3.6-11.7 kg/h, which corresponded to ϕ ratios of 0.95-3.1. Figure 3 shows the effect of the ϕ value on the combustion efficiency at several temperatures and Figure 4 shows, as an example, the gas composition obtained at the outlet of the FR at 1153 K as a function of ϕ value. Methane was fully converted for all tests, but CO and H₂ concentrations increased as solids circulation rate decreased. Using Ni-based oxygen carriers,

thermodynamic limitations prevent the full conversion of methane into CO₂ and H₂O, because the existence of small amounts of CO and H₂ at equilibrium condition. Combustion efficiencies and CO and H₂ concentrations close to equilibrium values were obtained working at high oxygen carrier to fuel ratios ($\phi > 1.5-2.5$), depending on the temperature, see Figures 3 and 4. A maximum value for efficiency of 99 % was obtained for ϕ about 3 for the three temperatures tested. Decreasing the ϕ value the combustion efficiency decreases because of the lower availability of oxygen in the FR. In a previous work¹¹ it was obtained that the average reactivity of solids decreases as the particles conversion increases, i.e. the ϕ value decreases, which agrees with results obtained in this work. Note that, assuming full oxidation of particles in the AR, the ϕ value is related to the variation of the solid conversion in the reactor, ΔX_s , and the conversion of the oxygen carrier in the FR, X_r , as follow

$$\Delta X_s = X_r = \frac{\eta_c}{\phi} \quad (10)$$

Figure 3. Effect of oxygen carrier to fuel ratio (ϕ) on the combustion efficiency (η_c) at three operation temperatures. Results from experimental test series A, where the solid circulation rate was varied. Methane flow = 50 L_N/h; $T_{FR} = 1073$ ($\diamond$), 1123 ($\triangle$), 1153 K ($\circ$); combustion efficiency at equilibrium condition (— —).

Figure 4. Effect of oxygen carrier to fuel ratio (ϕ) on the gas composition at the outlet. $T_{FR} = 1153$ K; Methane flow = 50 L_N/h; CO (Δ), H₂ ($\diamond$); equilibrium concentrations for CO (— — —) and H₂ (----).

Higher combustion efficiencies were obtained at higher temperatures as a consequence of the higher oxygen carrier reactivity. At ϕ values lower than 2, differences on the combustion efficiency with the temperature are evidenced by a sharp decrease in the combustion efficiency. This sharp decrease in the combustion efficiency was at lower ϕ values as the temperature increases.

Another experimental test series was carried out varying the fuel flow, but keeping the solids circulation rate approximately constant (≈ 10 kg/h). Figure 5 shows the combustion efficiency obtained as a function of the ϕ ratio when the fuel flow changed in the range 50-85 L_N/h (series B in Table 3). Qualitatively, the results were similar to those obtained when the solids circulation rate was varied. It was observed that for $\phi \approx 3$ the combustion efficiency was very close to the maximum allowed by the thermodynamic limit. Decreasing the oxygen carrier to fuel ratio decreases the combustion efficiency, being this effect more noticeable at lower ϕ ratios.

Figure 5. Effect of oxygen carrier to fuel ratio (ϕ) on the combustion efficiency (η_c) at three operation temperatures. Results from experimental test series B, where the fuel flow was varied. $T_{FR} = 1073$ ($\diamond$), 1123 ($\triangle$), 1153 K ($\circ$); combustion efficiency at equilibrium conditions (— — —).

It must be pointed out that experiments showed in Figure 5 were carried out at different fuel gas flow increasing the fuel concentration, but maintaining approximately constant the solids inventory in the FR (≈ 0.3 kg) and the air flow in the AR. Therefore, as the fuel flow increased, the ϕ ratio and the solids inventory in the FR per MW of fuel gas, m_{FR}^* , decreased. During operation it was possible to extract some of oxygen carrier particles coming from the AR, after cyclone separation. For every sample, the oxidation conversion was determined by TGA. It was found that the oxygen carrier was fully oxidized in the AR in all cases. So, the air to fuel ratio, λ , did not have any influence on the experimental results. Nevertheless, the decrease in ϕ and m_{FR}^* should produce a decrease in the combustion efficiency. So, from results showed in Figure 5 it is difficult to relate the effect of the fuel gas flow on the combustion efficiency to a change in the ϕ ratio, in m_{FR}^* , or in fuel concentration. To elucidate the importance of the solids inventory, a comparison between the results obtained from experimental test series A01-A11

1 (varying f_s) and series B01-B05 (varying f_{CH_4}) is shown in Figure 6 indicating also the m_{FR}^* value. It
 2 can be seen that, at a constant value for ϕ , the combustion efficiency for test series B, i.e. when the fuel
 3 flow changed, was lower than for experiments where the fuel flow was constant (series A). Differences
 4 between series A and B can be resumed in changes on the solids inventory per MW of fuel gas, m_{FR}^* ,
 5 and on the fuel concentration. By the one hand, the increase of the combustion efficiency when the ϕ
 6 value increases was higher when the fuel flow was changing (series B). Indeed, for $\phi > 1.5$ the effect of
 7 ϕ on the combustion efficiency was only noticeable when the methane flow was changed. This result
 8 agrees with results showed in a previous work¹¹ where it was showed that the average reactivity of
 9 particles in the reactor scarcely changed when the variation of the solid conversion in the reactor, ΔX_s ,
 10 was lower than 0.5-0.6, corresponding to $\phi > 1.5-2$. This fact suggests that for ϕ values higher than 1.5-2
 11 an increase in the solids inventory in the FR should have a higher influence on the combustion
 12 efficiency than an increase in the solids circulation rate. Moreover, the combustion efficiency probably
 13 should be some higher if FR temperature was above 1153 K. For comparison purposes, Figure 6 also
 14 shows the combustion efficiency obtained using several NiO-based oxygen carriers by other authors,<sup>19-
 15 24</sup> which will be discussed later. By the other hand, a higher concentration should increase the
 16 combustion efficiency when m_{FR}^* was constant, whereas a m_{FR}^* decrease affects negatively to the
 17 combustion efficiency. From results showed in Figure 6 can be concluded that the negative effect of the
 18 decrease of m_{FR}^* on the combustion efficiency was higher than the positive effect of the increase of fuel
 19 concentration. Therefore, it can be concluded that the solids inventory, m_{FR}^* , and fuel reactor
 20 temperature has a high relevance on the combustion efficiency, whereas the solids circulation rate
 21 became also important at $\phi < 1.5-2$.
 22
 23

Figure 6. Effect of oxygen carrier to fuel ratio (ϕ) on the combustion efficiency (η_c) for experimental series A ($\circ$) and B (Δ), see Table 3. Values indicate the solids inventory per MW, m_{FR}^* , in series B. $T_{FR} = 1153$ K; combustion efficiency at equilibrium conditions (— — —). For comparison purposes also are shown values estimated from literature data obtained using Ni60-NiAl:FG²⁴ ($\blacklozenge$) and Ni60-MgAl:FG²³ ($\blacktriangle$) in a 300 W_{th} CLC facility, using Ni40-NiAl:FG²⁰ ($\diamond$) and Ni60-NiAl:SP²¹ ($\square$) in a 10 kW_{th} prototype, and using Ni60-B:MM²⁷ ($\bullet$) in a 1.5 kW_{th} prototype.

Effect of CLC operation on oxygen carrier particles.

As above mentioned, oxygen carrier particles have been fluidized in hot conditions for approximately 100 h, of which 70 h were with methane combustion. These particles were not replaced during the combustion tests, and new material was not added at any time. Agglomeration or defluidization was never detected using this oxygen carrier during CLC operation. A total mass loss in the system of 19 g –1.6 wt%– was observed after experimental tests, which 0.6 wt% was elutriated during the first moments at hot conditions because of its small initial size. Rest of mass loss (1 wt%) was related to attrition of particles, corresponding to a value of 0.01 wt%/h. Figure 7 shows the particle size distribution for fresh and used particles. Lost of finest particles scarcely had any effect on the particle size distribution. Physical and chemical properties of the

oxygen carrier particles after the CLC operation were compared to those of fresh particles. No major changes in the porosity, density, BET surface area or mechanical strength were observed in the particles after they were used in the CLC system (see Table 2). SEM-EDX pictures of fresh and used particles can be seen in Figure 8. No major differences could be observed in the surface texture and the solid structure, and avoidance of cracks was verified. Ni distributed throughout the inner the particle was found in all the samples, fresh and used, by EDX analysis in the cross section of particles. However, it was found little clusters of NiO –up 10 μm of size– where Ni was more concentrated than in surroundings, see brightness areas in SEM pictures. The size of this NiO grains remained constant after operation in the CLC prototype, that is, there was not evidence of redistribution or migration of Ni sites during the redox cycles. Moreover, not signs of agglomeration were observed in SEM pictures for used particles, agreeing to the avoidance of agglomeration or defluidization in the CLC prototype. These results suggest that this oxygen carrier could have a high durability, being a suitable oxygen carrier for a CLC system.

Figure 7. Particle size distribution of fresh material (—) and particles used for 100 h in the CLC system (---).

1

2

3 **Figure 8.** SEM image of (a) fresh particles and (b) used particles for 100 h in the CLC prototype and
4 EDX analysis for Ni distribution in the cross section of the particle.

5

Effect of operating conditions on oxygen carrier particles.

A study on chemical properties was carried out for different samples of solids taken during solid circulation measurement at the cyclone outlet. In all cases, XRD analysis showed the appearance of fully oxidized phases, i.e. NiO and NiAl₂O₄. These phases were also found for fresh particles. The relative amount of NiO and NiAl₂O₄ was obtained through TPR analysis using H₂ as reducing agent. As an example, Figure 9 shows the results of the H₂-TPR analysis performed over different solid samples corresponding to different ϕ values. In line with data reported by Villa et al.³¹ the TPR spectra showed a profile with two separate peaks: a H₂ consumption peak centered in the low temperature range 650–900 K and a high temperature peak with maximum near 1150-1200 K. The low temperature peak is well known to correspond to the reduction of Ni²⁺ in the free NiO phase, whereas the high temperature peak is attributed to the reduction of Ni²⁺ in the NiAl₂O₄ spinel phase. The complexity of the low temperature peaks likely is ascribed to the presence of different sizes for NiO crystallites, which affects to the nucleation rate.⁵⁶ In this sense, TPR profiles are consistent with XRD data which indicate the presence of both free NiO and NiAl₂O₄ phases. Figure 9 also shows the normalized weight, W_N, of samples during TPR carried out in TGA. The normalized weight is defined by

$$W_N = \frac{m - m_f}{m_o - m_f} \quad (11)$$

where m = instantaneous mass, m_o = initial mass, and m_f = final mass at complete reduction of the oxygen carrier.

It can be observed that the fraction of oxygen carrier reduced at low or high temperature depends on the ϕ value used in the CLC test. At 900 K, free NiO has been fully reduced and NiAl₂O₄ is not reduced at temperatures below 1050 K. The value taken for the normalized weight between these temperatures is related to the Ni fraction present as NiAl₂O₄ phase for each sample of the oxygen carrier, $w_{\text{NiAl}_2\text{O}_4}$, being the Ni fraction as free NiO calculated as $w_{\text{NiO}} = 1 - w_{\text{NiAl}_2\text{O}_4}$.

Figure 9. Temperature-programmed reduction with hydrogen of fresh particles and different samples corresponding to different operating conditions. (a) H₂ consumption by TPR; (b) normalized weight-loss profiles for H₂-TPR in TGA.

Figure 10 shows the relative fraction of total Ni presents as free NiO phase for fresh particles and used particles in the CLC tests at 1153 K as a function of ϕ ratio. All used particles samples, which were extracted after the cyclone separation at the AR exit, were found fully oxidized, agreeing to results obtained from XRD analysis. For fresh particles, the relative amount of Ni presents as free NiO was $w_{\text{NiO}} = 65\%$. For used particles, on increasing the ϕ value, a decrease of the relative abundance of free NiO phase was observed, and therefore the amount of NiAl₂O₄ increased. Likely, the lower extent of reduction reached in the FR with an increase of the ϕ value affects on the phase composition of the oxygen carrier particles. In this sense, Figure 10 also shows the solid conversion reached in the FR for

1 the different experimental tests calculated using eq 10, which corresponded to metallic Ni formed in the
2 FR. Although the conversion curve follows the same tendency than the relative abundance of free NiO,
3 the conversion values are higher than the NiO fraction as free NiO phase. Likely, this fact is because a
4 fraction of the reduced Ni is converted into NiAl_2O_4 during the solids oxidation in the AR which had a
5 residence time in the range 3-10 min. From these results it was estimated that about a 75% of reduced
6 Ni is oxidized into free NiO, whereas the rest is transformed into NiAl_2O_4 phase. This fact was
7 confirmed by new TGA experiments carried out with reduced particles extracted from the FR. These
8 particles were oxidized in air at 1223 K. Full oxidation was achieved in less than 10 seconds, but
9 oxidation conditions were maintained for times varying between 3 and 30 minutes. After oxidation, NiO
10 and NiAl_2O_4 fraction was determined by TPR analysis. In all cases analyzed, about 25% of Ni initially
11 present in the reduced samples was oxidized into NiAl_2O_4 , and the rest remained as NiO. Previous
12 work³⁴ suggests that this fraction could depend on the oxidation temperature and the NiO content.
13

14
15 **Figure 10.** Fraction of Ni as NiO or NiAl_2O_4 in the oxygen carrier ($\circ$) as a function of the oxygen
16 carrier to fuel ratio (ϕ). Fraction of NiO in fresh particles (.....); fraction of NiO reduced in the FR, i.e.
17 X_r (---); and values for 75% of NiO reduced in the FR (—).
18

Since reactivity of NiO phase is different from that of NiAl₂O₄ phase,³¹ reactivity for oxygen carrier should change with ϕ , because of its effect on the amount of NiAl₂O₄ formed. To confirm this fact, reactivity of reduction reaction for fresh and used particles in CLC at different operating conditions was determined in TGA at 1223 K, using 15 vol% CH₄. Figure 11 shows the conversion-time curves correlated with the conversion of solids in the FR, X_r , calculated using eq 10. The reduction of the oxygen carrier particles proceeds in two stages according to the fast reduction of the free NiO phase and the slower reduction of NiAl₂O₄. The reactivity of each sample depends on the experimental conditions used in the CLC tests: higher the conversion of solids in FR, higher the conversion level where the reaction is fast, which agrees with the results showed above about the effect of ϕ on the amount of NiO and NiAl₂O₄ in the solids. Moreover, the reactivity for used particles was lower than for fresh particles, because of the higher amount of NiAl₂O₄ in used particles with respect to fresh particles.

Figure 11. TGA reactivity data for reduction of fresh particles (---) and used particles in the CLC system corresponding to different X_r values (—). Temperature = 1223 K; CH₄ = 15 vol%.

In view of the fact that particles can improve their reactivity when the reduction degree increases, a new test was carried out in the 500 W_{th} CLC prototype (test C01 in Table 3). Particles in the CLC were

fully reduced using H_2 as fuel gas in the FR and nitrogen as fluidizing agent in the AR, and later particles were fully oxidized replacing nitrogen by air in the AR. After this activation step, CLC was running normally using 30 vol% CH_4 in the FR (1153 K), air in the AR (1223 K), and $\phi = 2.7$. Initially, particles showed high reactivity and the free NiO phase fraction was 47 wt%, but particles lost reactivity with time. After three hours of operation, the free NiO phase fraction was 29 wt%, a similar value that this showed in Figure 10 for $\phi = 2.7$. As previously mentioned, about 75% of the Ni reduced in the FR was oxidized into free NiO. Both, the rest of metallic Ni and the not reduced NiO in the FR had enough time at high temperature in the CLC system to promote the $NiAl_2O_4$ phase. Consequently, the NiO- $NiAl_2O_4$ ratio in the oxygen carrier stabilized in a fixed value depending on the solid conversion in the FR, which was related to the ϕ value.

Finally, CLC test series gave the same results for NiO- $NiAl_2O_4$ ratio in the particles either increasing or decreasing the value for ϕ , indicating the reversibility of Ni between NiO and $NiAl_2O_4$ phases. From the results showed in this work we concluded that a fraction of $NiAl_2O_4$ present in the oxygen carrier, which depends on the ϕ value, is active for oxygen transference in the FR. Therefore, $NiAl_2O_4$ can not be considered as an inert material in this kind of oxygen carrier, as previously was found.³⁴

Considerations about design criteria. The use of a specific oxygen carrier has important implications for a CLC system. The reduction and oxidation reactivity of solids determines the solids inventory in the fuel and air reactors, respectively, to reach the full conversion of fuel gas.¹¹ From the results obtained in this work, a combustion efficiency about 99% was obtained for 50 L_N/h CH_4 using a solids inventory of 300 g of $Ni_{18-\alpha}Al_{HI}$ oxygen carrier in the FR, which corresponds to $m_{FR}^* \approx 600$ kg/ MW_{th} . A number of publications have reported data for successfully methane or natural gas combustion in a continuously operated CLC system, see Table 4.¹⁹⁻²⁷ From the results showed in these works, and for comparison purposes, the combustion efficiency was estimated as a function of the ϕ ratio –see Figure 6 for Ni-based oxygen carriers– and the solids inventory in the FR. In general, high combustion efficiencies, close to the value for thermodynamic equilibrium, were obtained except for the

oxygen carrier Ni60-B:MM because of its lower reactivity.²⁷ During tests in the 500 W_{th} unit showed in this work, the circulation rates were in the range $\phi=1-3$, lower than those used in the 10 kW_{th} prototype ($\phi=5$)^{20,21} or in the 300 W_{th} facility ($\phi=10-50$)^{23,24} at CUT. In spite of this difference, Figure 6 shows that the combustion efficiency obtained in the 500 W_{th} unit was in line with the obtained in the other facilities using different NiO-based oxygen carriers. The solids inventory to get a combustion efficiency of 99% for different oxygen carriers is showed in Table 4. It should be pointed out that the numbers for the solids inventories are not directly comparable among them, since differences in the fluidization conditions at different CLC prototypes may have important effects on the mass transfer resistance between gas and solids. Nevertheless, the numbers give a first impression of the solids inventories that could be needed. A solids inventory about 600 kg/MW_{th} was needed for Ni18- α Al:HI oxygen carrier, whereas using Ni-based particles prepared by freeze-granulation or spin-flash method the solids inventory was in the range 335-630 kg/MW_{th}. For Ni60-B:MM it would be necessary a solids inventory higher than 760 kg/MW_{th} to get combustion efficiencies close to equilibrium conditions. Nevertheless, it is remarkable the differences in the amount of Ni metal from these oxygen carrier, $m_{Ni,FR}^*$, which is the most expensive material to prepare the oxygen carrier. Based on the amount of Ni in solid particles per MW_{th}, the Ni inventory for Ni18- α Al:HI was the lower among them, see Table 4. However, it is likely that high efficiencies can be achieved with lower amounts of solids for Ni40-NiAl:FG and Ni60-NiAl:SP particles, because the FR was oversized in the 10 kW_{th} prototype at CUT.

Also for methane combustion, oxygen carrier particles based on Cu, Mn and Fe oxides have been successfully used in different CLC prototypes.^{22,25,26} A combustion efficiency of 99% was obtained using solids inventories about 300 kg/MW_{th} for Cu-based OC, 600 kg/MW_{th} for Mn-based OC, and 1200 kg/MW_{th} for Fe-based OC. In spite of the relative high reactivity of the impregnated NiO-based OC the solids inventory was in the middle of this range, because of the development of the low reactive NiAl₂O₄ spinel phase during the preparation or operation in the CLC system. Lower solids inventory could be obtained stabilizing the inert solid, Al₂O₃, to avoid the NiAl₂O₄ formation. For example, the use of MgAl₂O₄ as support material has been reported in the literature to obtain suitable NiO-based

oxygen carrier by coprecipitation,³¹ impregnation,^{34,42} freeze granulation²⁸ or solution combustion synthesis.³⁷

Table 4. Operating conditions to obtain a combustion efficiency of 99% using different oxygen carrier particles and CLC prototypes.

Oxygen carrier	CLC system	T _{FR} (K)	ϕ	m _{FR} [*] (kg/MW _{th})	m _{Me,FR} [*] (kg/MW _{th})	Reference
Ni18- α Al:HI	500 W	1153	3.09	600	85	This work
Ni40-NiAl:FG	10 kW	1073-1173	5	335	170	[20]
Ni60-NiAl:SF	10 kW	1123-1203	5	335	200	[21]
Ni60-MgAl:FG	300 W	1123	20	630	300	[23]
Ni60-NiAl:FG	300 W	1123	10	400	240	[24]
Ni60-B:MM	1.5 kW	1123	>1.9	>760	>360	[27] ^(a)
Ni60-B:MM	50 kW	1023	-	1250	590	[19]
Cu14-Al:IMP	10 kW	1073	1.3	300	34	[22]
Mn40-MgZr:FG	300 W	1223	4	600	170	[25]
Fe60-Al:FG	300 W	1223	>8	>1200	>500	[26] ^(a)

^(a) Not was obtained η_c as high as 99%

The amount of the oxygen carrier in the AR of the 500 W_{th} CLC facility was about 0.5 kg for all experimental tests, where the fuel flow varied in the range 85-50 L_N/h. Referred to 1 MW_{th}, the solids inventory in the AR was 590-1000 kg/MW_{th}, but likely a smaller amount of solids would be necessary because the oxygen carrier was fully oxidized for all experimental tests in the AR, indicating that the AR was oversized.

Additionally, the solid circulation in a CLC plant must be fixed to fulfil the mass and energy balances in the system. The solid circulation is limited by the transport capacity of the riser. The limit of the circulation rate in a CLC plant is not clear, but a value of 16 kg s⁻¹ per MW_{th} of methane can be taken as the maximum circulation rate feasible in a CLC plant without increased costs and with commercial

experience.¹¹ For Ni18- α Al:HI oxygen carrier this value correspond to an upper limit for ϕ about 8, giving by the riser transport capacity. Moreover, the energy balance must be specially considered when the reaction in the FR is endothermic, as it is the case of the reduction of NiO by methane. In this case, the FR is heated by the circulating solids coming from the AR at higher temperature. A minimum circulation rate of solids is necessary in order to maintain the temperature in the FR, which depends on the oxygen transport capacity, i.e. the metal oxide type and content. For the use of the oxygen carrier considered in this work (18 wt% NiO) in a CLC system using methane as fuel gas, a minimum value for ϕ about 2 must be attained to maintain a temperature difference of 50 K between the AR and FR. From the results showed in this work it can be concluded that a solids circulation rate corresponding to an oxygen carrier to fuel ratio $\phi = 1.5$ was enough to get high combustion efficiency, whereas the oxygen carrier to fuel ratio must be in the range $\phi = 2-8$ in a CLC system using Ni18 α -Al:HI oxygen carrier. Therefore, in this range for ϕ , high combustion efficiencies close to the equilibrium value were obtained in the CLC prototype.

CONCLUSIONS

A continuous CLC plant (500 W_{th}) has been used to know the effect of operational conditions on methane combustion in a CLC system using a Ni-based oxygen carrier. The oxygen carrier used in this work was prepared by HIWI method on α -Al₂O₃, containing 18 wt% NiO. Different experimental tests series were done varying the solids circulation rate or the methane flow. The 500 W_{th} CLC prototype was easy to operate, and steady state conditions were rapidly reached and maintained along each experimental test. No methane was detected at the FR exit, being CO and H₂ the unconverted gases. The main operation variables affecting the combustion efficiencies, i.e., the oxygen carrier to fuel ratio, the solids inventory and the FR temperature, were analyzed. Tests carried out during continuous operation in the CLC prototype have allowed us to determine the conditions necessary to obtain a high efficiency during the methane combustion using this Ni-based oxygen carrier. At 1153 K, an oxygen carrier to fuel ratio, ϕ , higher than 1.5, and a solid inventory in the FR of 600 kg per MW_{th} were necessary to reach

1 combustion efficiencies close to the maximum allowed by the thermodynamic constraint. The solids
2 inventory and fuel reactor temperature had a high relevance on the combustion efficiency, whereas the
3 solids circulation rate became also important at $\phi < 1.5-2$.

4 During 100 hours of operation, the oxygen carrier particles never showed agglomeration problems or
5 carbon deposition in the FR. The attrition rate was about 0.01 wt% per hour. No changes in the physical
6 properties of the particles were observed. It was found that Ni in the oxygen carrier was distributed
7 between two different phases: free NiO and NiAl₂O₄. Both phases were active in the CLC prototype to
8 transfer oxygen from air to fuel gas, but NiAl₂O₄ was less reactive than free NiO. The relative amount
9 of NiAl₂O₄ decreased as the solids conversion in the fuel reactor increased, i.e. the solids circulation
10 rate decreased. As the reactivity of NiAl₂O₄ was lower than that for free NiO, the solids circulation rate
11 affected negatively to the oxygen carrier reactivity. As consequence, for this kind of oxygen carrier
12 materials, the reactivity must be evaluated as a function of the operational conditions in a CLC system.
13 The results obtained in this work showed that the use of a nickel oxygen carrier prepared by
14 impregnation is suitable for methane combustion in a continuously operated CLC system.

15
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NOMENCLATURE

- f_{CH_4} = flow of methane at the reactor inlet ($\text{L}_\text{N} \text{ h}^{-1}$)
- f_S = flow of solids in the CLC system (kg h^{-1})
- f_S^* = flow of solids in the CLC system referred to 1MW_th ($\text{kg s}^{-1} \text{ MW}^{-1}$)
- F_i = molar flow of the i compound (mol s^{-1})
- m = instantaneous mass of the oxygen carrier (kg)
- m_f = final mass at complete reduction of the oxygen carrier (kg)
- m_o = initial mass of the oxygen carrier (kg)
- m_FR^* = solids inventory in the fuel reactor referred to 1MW_th (kg MW^{-1})
- $m_\text{Me,FR}^*$ = metal inventory in the fuel reactor referred to 1MW_th (kg MW^{-1})
- $\dot{m}_\text{O}$ = oxygen transfer rate in the AR or FR (at-gr O s^{-1})
- R_OC = oxygen transport capacity of the oxygen carrier
- T = temperature (K)
- w_NiO = fraction of Ni as NiO phase in the oxygen carrier
- $w_\text{NiAl}_2\text{O}_4$ = fraction of Ni as NiAl_2O_4 phase in the oxygen carrier
- w_0 = NiO content in the oxygen carrier (wt%)
- W_N = normalized weight
- x_i = molar fraction of the gas i
- X_r = reduction conversion of the oxygen carrier in the FR
- Greek symbols
- ΔX_S = variation of the solid conversion
- ϕ = oxygen carrier to fuel ratio, as defined in equation 4
- Φ_ox = stoichiometric index, as defined in equation 9

- 1 λ = air excess ratio, as defined in equation 3
- 2 η_c = combustion efficiency, as defined in equation 5
- 3
- 4 Subscripts
- 5 AR = air reactor
- 6 FR = fuel reactor
- 7 OC = oxygen carrier
- 8 S = solids
- 9
- 10
- 11

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