Final publishable summary report

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Project full name: Innovative Oxygen Carriers Uplifting chemical-looping combustion

Executive Summary

In previous EU-projects, chemical-looping combustion for gaseous fuels has developed from paper concept to demonstration in sizes up to 120 kW fuel power. Satisfactory fuel conversion performance has been achieved with several nickel-based oxygen carrier materials. However, nickel-based materials are expensive and require special environmental/safety precautions. The INNOCUOUS project involved a focused search for alternative materials with comparable performance to nickel. This activity is without doubt the most important task to improve the prospects for large-scale deployment of this technology. Two main approaches have been examined: i) nickel-free materials which may or may not take advantage of direct release of molecular oxygen from the solids (CLOU) and ii) the mixed oxides concept, using mainly non-nickel materials with high reactivity towards CO/H2, together with a minor fraction of particles of reduced nickel content acting as reforming catalyst (i.e. transferring CH4 to CO/H2).

In total, more than 150 particle samples have been manufactured by commercially available methods (spray drying or impregnation). Examined materials used manganese, iron or copper oxide as main active component, in some cases with addition of small amounts of nickel oxide. Many materials involved several anions present in the form of combined oxides, such as for example calcium manganite. Some materials used inert support such as alumina or zirconia to achieve sufficient strength and reactivity.

All materials were characterized and tested either in batch reactor or by thermogravimetric analysis. 16 promising materials were selected and examined in small continuously operating units (300-500W). Out of these four materials and one material mixture were selected and examined under realistic conditions in a larger 120 kW unit. Two of these were also thoroughly examined in an intermediate sized 10 kW unit, and by comprehensive testing in laboratory. The final result of the oxygen carrier development process was a few materials with similar or better reactivity than nickel oxide and high resistance to attrition based on cheap and harmless raw materials such as manganese, iron, calcium and magnesium. Successful operation with complete fuel conversion and complete carbon dioxide separation was achieved with nickel free oxygen carriers both in 10 kW and 120 kW reactors.

An important goal of the Innocuous project was to find materials than nickel oxide materials, representing the state of art. This has been fulfilled as materials have been demonstrated that:

- show complete gas conversion, in contrast to NiO materials being limited to 98-99% conversion.
- are composed of raw materials very much cheaper than nickel oxide.
- are not associated with significant risks for health and environment in contrast to nickel.
- show low attrition rates, comparable to previous results with nickel oxide materials.

In addition to experimental verification of chemical-looping combustion with oxygen carriers containing no or very little nickel, considerable effort was put into developing manufacturing processes for oxygen carriers. Two methods was examined, spray drying and impregnation. In order to operate the largest units about 100 kg of active material was required, and such samples were successfully manufactured over the course of the experiments using both methods. Experience from this process has been used to make a cost realistic estimation for oxygen carrier materials to a full-scale chemical looping boiler.

Another part of the project has concerned the development of a process model for chemical-looping combustion. This constitutes a useful tool when designing reactor systems for the process.

Based on obtained results, an overall process integration and design for a 10 MW natural gas fired chemical looping boiler has been proposed. It is concluded that due to the need of two reactors, the divided flue gas streams and the oxygen carrier system a chemical looping boiler would be more expensive than a common gas fired boiler. The process as a whole looks feasible and attractive though, since complete carbon dioxide sequestration would be achieved at reasonable cost.

Summary description of project context and objectives

The main difficulty with carbon capture is high energy penalty and costs for gas separation processes, common for pre-combustion capture, post-combustion capture and oxyfuel combustion. The fundamental novelty of chemical looping combustion (CLC) is that no gas separation step is needed at all. Metal oxides are used to transport oxygen from an air reactor to a fuel reactor. The principle ideally allows elimination of the capture penalty. Circulating fluidized bed (CFB) technology is used, for which there is long commercial experience in power industry with conventional combustion. Moreover, in contrast to pre- and post-combustion capture, chemical-looping combustion readily reaches capture rates of 100%.

In previous EU-projects, chemical-looping combustion for gaseous fuels has developed from a paper concept to actual operation at 120 kW fuel power. Satisfactory fuel conversion performance has been achieved with several nickel-based oxygen carrier materials. However, nickel-based materials are expensive and require special environmental/safety precautions. The INNOCUOUS project involved a focused search for alternative materials with comparable performance to nickel. This activity is without doubt the most important task to improve the prospects for large-scale deployment of this technology. Two main approaches have been examined:

(i) nickel-free materials which may or may not take advantage of direct release of molecular oxygen from the solid (CLOU)

(ii) the mixed oxides concept, using mainly non-nickel materials with high reactivity towards CO/H2, together with a minor fraction of particles of reduced nickel content acting as reforming catalyst (i.e. transferring CH4 to CO/H2).

The project has utilized a mixture of experimental and theoretical activities, with focus on experimental verification of the process using selected oxygen carrier materials. It is a joint project, involving the following organizations:

- Chalmers University of Technology (Chalmers)
- Agencia Estatal Consejo Superior De Investigaciones Científicas (CSIC)
- Technische Universität Wien (TUV)
- Flemish Institute for Technological Research (VITO)
- Shell Global Solutions International B.V. (Shell)
- Johnson Matthey PLC. (JM)
- Josef Bertsch Gesellschaft m.b.H & Co Bertsch (Bertsch)

The work has been conducted within 7 work packages, which are listed and briefly explained below:

- *WP 1 Development of new combined oxide materials without nickel*

Basic experimental examination characterisation of oxygen carriers without nickel. While a wide approach has been used focus was on oxides with several cations present in one single phase, such as for example calcium manganite. This concept is referred to as “combined oxides” in the report.

- *WP 2 Highly reactive material systems with low nickel content*

Basic experimental examination characterisation of oxygen carriers with very low content of nickel. The basic idea was to utilize the catalytic properties of nickel, while using another active phase as bulk oxygen carrier. This concept is referred to as “mixed oxides” in the report.

- *WP 3 Innovative development of scale up ready particle preparation routes*

The aim was to assess existing and innovative approaches for the preparation of oxygen

Carrier paricles suitable as bed material in fluidized beds. Preparation by both spray-drying and impregnation techniques was used. All materials for WP1, WP2 and WP4 was produced within this work package.

- *WP 4 Testing of new particles under relevant conditions*

This work package involved experiments in continuously operating chemical looping combustion reactors. The nominal thermal power of used reactors were 300W, 500W, 10 kW and 120 kW, each size required an increasing amount of oxygen carriers. For the largest reactor batches of more than 100 kg solids were manufactured. Testing in the larger units which are of relevant design and use realistic gas velocities is a good indication for the performance of the different materials.

- *WP 5 Overall process integration and CLC next scale design*

The current status of chemical looping combustion is reviewed and updated with insights from experimental testing and modelling. A bulk design of the fluidized bed reactor system was proposed and optimized. A plant layout for a 10 MW chemical looping boiler was developed, and a detailed assessment of economics and environmental impact was conducted.

- *WP 6 Dissemination of results*

Research results were presented to stakeholders and the public via publication in scientific journals, participation in international conferences, by arranging two public dissemination workshops, and by operating a project web site.

- *WP 7 Coordination*

The project was coordinated by Chalmers.

The project was successfully conducted, and all goals were met. In total, more than 150 oxygen carrier materials have been proposed and manufactured by commercially available methods (spray drying or impregnation). Examined materials used manganese, iron, copper or copper oxide as main active component, or small amounts of nickel oxide. Some materials used inert support such as alumina or zirconia to achieve sufficient strength and reactivity. Other materials involved several anions present in the form of combined oxides, such as for example calcium manganite, i.e. $CaMnO_3$.

All manufactured materials were also characterized and tested either by redox experiments in batch reactor or by thermo gravimetric analysis. Further analysis such for example as x-ray diffractometry, crushing strength, and morphological analysis was also conducted. A total of 16 promising oxygen carrier materials based on widely different compositions were selected and examined in small continuously operating units (300-500W). From the results of these tests several systems were deemed highly promising, and six particles were judged to fulfil all success criteria set-up for a viable oxygen carrier, and thus selected to be included in a portfolio of oxygen carriers. Out of these four materials and one material mixture were selected and examined under realistic conditions in the large 120 kW unit. Two of these were also thoroughly examined in an intermediate sized 10 kW unit, and by comprehensive testing in laboratory. Two materials, based on the perovskite $CaMnO_3$, showed remarkable reactivity, and full fuel conversion was achieved for the first time in the 10 kW continuous unit at Chalmers and the 120 kW unit in Vienna. Thus the main goal of the project was clearly met, i.e. oxygen carriers were developed which showed similar or better reactivity than nickel oxide and high resistance to attrition based on cheap and harmless raw materials. In particular, spray-dried particles materials based on calcium manganite of perovskite structure showed very promising behaviour.

In addition to experimental verification of chemical-looping combustion with oxygen carriers containing no or very little nickel, considerable effort was also put into developing manufacturing processes for oxygen carriers. Two methods was examined, spray drying and impregnation. Optimization of these manufacturing processes was performed during the project in order to effectively scale-up to production of batches of more than 100 kg, amounts which are needed in order to operate the largest unit, and such samples were successfully manufactured over the course of the project using both methods. Experience from this process has been used to make a cost realistic estimation for oxygen carrier materials to a full-scale chemical looping boiler. In this techno-economic analysis it was determined that the the lab-scale production routes used here are relevant to those used widely in the solids processing industries and there does not appear to be any significant technical barriers in the manufacturing process. The spray-drying route appeared to be most cost-effective, although this could be dependent on the materials employed and the process parameters, and no firm conclusions could be drawn with respect to optimal route of production. However, it was established that the raw material cost is critical, hence again providing incentive to find oxygen carriers utilizing cheap materials. Further, if the European Union enacts stricter regulations with respect to use of Ni, this could have profound negative effects on costs for production of materials with Ni, hence again, supporting the quest for alternatives to this toxic raw material.

Another part of the project has concerned the development of a process model for chemical-looping combustion. This constitutes a useful tool when designing reactor systems for the process. Based on obtained results, an overall process integration and design for a 10 MW natural gas fired chemical looping boiler have been proposed. It is concluded that due to the need of two reactors, the divided flue gas streams and the oxygen carrier system a chemical looping boiler would be more expensive than a common gas fired boiler. However, the process as a whole looks feasible and attractivem since complete carbon dioxide sequestration would be achieved at reasonable cost.

The cornerstone of the chemical-looping technology is the development of oxygen carriers which can have a high reactivity, meaning low bed inventory, in combination with long lifetime. Further, the cost of the oxygen carrier could be an important part of the total cost for the capture process, and thus needs to be kept as low as possible. This alone makes Ni relatively unattractive, due to the much higher material cost compared to other common transition metals, i.e. Cu, Fe and Mn. The added disadvantage with Ni is that it probably is not feasible to utilize it in a new industrial process in the European Union provided that there is no other alternative. Chemical-looping combustion has been pointed out by many researchers as the most viable alternative for carbon capture from natural gas, but has had the drawback that Ni has been the only proven alternative as oxygen carrier. The INNOCUOUS project has taken the technology to the next level of development, in the development of new and novel oxygen carriers which have proven potential at realistic conditions. This is a major breakthrough. The techno-economic studies of the process and oxygen carrier scale-up which was part of this project as well, confirm the great potential of the technology.

Description of main S & T results/foregrounds

WP1 Development of new combined oxide materials without nickel

The successful development of nickel free oxygen-carrier materials would give important cost reductions compared to using nickel. This is valid both for the material costs, but also for the solids handling where nickel materials would need additional precautions to assure health and safety aspects. The focus of WP1 therefore was to reduce costs and environmental risks of the technology by investigating alternatives to nickel oxide. Previous work on oxygen carrier development has mainly focused on pure oxides, i.e. oxides of nickel, copper, iron, manganese, normally using a support of inert oxides, e.g. alumina oxide. However, little work has been done on what is here called "combined oxides", by which is meant combinations of oxides forming new compounds, e.g. combining manganese and calcium to $CaMnO_{3-\delta}$. This should not be confused with the concept in developed in WP2, "mixed oxides", in which different oxides are mixed, either as different particles, or in the same particle, but still remaining as separate compounds. Especially interesting are combined oxides based on manganese oxide, a class of materials with potentially high reactivity and CLOU properties. It has been found that a number of oxides, e.g. Fe, Mg, Ni, Si etc., can be combined with manganese and raise the oxidation state of manganese in such a way that oxygen can be released and also that these materials can achieve very high reactivity towards methane.

The general methodology for evaluation oxygen carrier materials can be seen in Figure 1 below. The oxygen carrier composition was proposed based on earlier results or thermodynamic calculations. The oxygen carriers were prepared by the different partners: spray-drying (VITO) and impregnation (CSIC, JM). Each material was evaluated in batch fluidized bed reactors or thermogravimetric analyzers utilizing conditions relevant for CLC with respect to gaseous components and concentrations as well as temperatures. The crushing strength of the material is also evaluated. If the materials were deemed promising from batch testing, samples were prepared for testing in continuous units of smaller size of a few hundred watts power, available both at Chalmers and at CSIC.

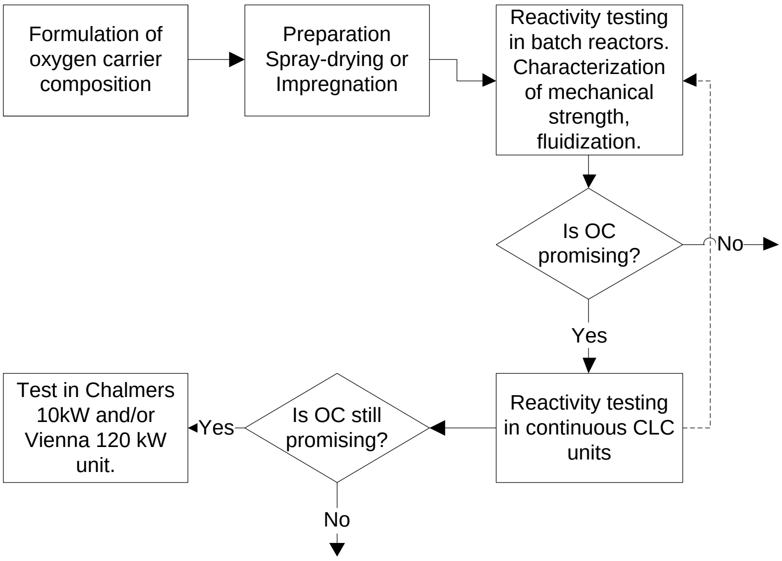

Figure 1.1 Working principle of oxygen carrier screening.

WP1 concerns the upper three boxes in figure 1.1. The main goal is to find highly reactive oxygen carriers based on combined oxides, and suitable for chemical-looping combustion. Materials which are considered promising up to this point was then further examined, but these activities belong in WP4.

A total of 60 compositions were spray-dried at VITO in WP3. Each material was calcined at a minimum of two temperatures, resulting in a total of 130 evaluated oxygen carriers based on spray-drying. Table 1 gives an overview of the types of spray-dried oxygen carriers which have been prepared, and also an indication of methane conversion as determined in a batch fluidized bed reactor. Detailed description of all examined materials and the experimental methodology can be found in the corresponding deliverables (D1.1 First selection of materials, D1.2 First results from reactivity testing, D1.3 Mid-term results material development and first selection for scale-up, D1.4 Material development results and second selection for scale-up).

Table 1.1 Overview of the type of oxygen carriers evaluated in the project and some indicative numbers of methane conversion as determined in batch tests.

Oxygen carrier	Solids inventory	Average fuel
1) NiO (VITO-A) (ref)	6 kg/MW	80-90%
2) $CaMn_yM_{1-y}O_{3-\delta}$	57 kg/MW	86-99%
3) $Mn_{3-y}Mg_yO_4$	57 kg/MW	46-84%
4) CuO + support material	57 kg/MW	83-100%
5) $(Mn_ySi_{1-y})O_x$	57 kg/MW	73-98%
6) $Fe_yMn_{1-y})Ti_xO_z$	57 kg/MW	4-76%
7) $(Fe_yMn_{1-y})Si_xO_z$	57 kg/MW	45-71%

* Obtained at 950°C and at an average mass-based conversion interval of 1 or 2%.

All types of materials in Table 1.1 have so called oxygen uncoupling properties (CLOU), i.e. they can release gas phase oxygen directly in the fuel reactor. In order to compete with Ni-based oxygen carriers, it was deemed important to produce such materials, as oxygen uncoupling is likely will enhance overall combustion performance considerably. As the mechanism for reaction may be different than direct gas-solid reactions, as in CLC, the methane conversion data is simply illustrated as conversion for a certain bed inventory of particles, i.e. kg/MW.

Out of the 130 different particles produced by spray drying, 10 were chosen for further examination in a continuously operating reactor system with the nominal thermal power of 300 W. Based on these experiments two spray dried particles was chosen for further experiments in 10 kW and 120 kW reactors. Operation in continuous reactors are described under the heading WP4.

The two most promising spray-dried materials based on experiments in batch reactor (WP1) and continuous operation (WP4), were variants of the calcium manganite perovskite structure (CaMnO3) in which small amounts of manganese had been substituted for magnesium and titania. Henceforth these two materials will be called C14 ($CaMn_{0.9}Mg_{0.1}O_{3-\delta}$) and C28 ($CaMn_{0.775}Mg_{0.1}Ti_{0.125-\delta}$). Both these particles were capable of releasing gas phase O_2 and had reactivity with natural gas in the same range as the NiO-based reference particle VITO-A. The raw materials are much cheaper than NiO and also environmentally benign. Experiments in continuously operating reactors reinforced these impressions, and also verified that the resistance to attrition of this family of materials is adequate. See WP4 for more about this.

The final part of WP1 considered detailed investigation and characterisation of the materials chosen for scale-up. The objective was to gain a better understanding of the materials selected for scale-up (D1.5 Comprehensive testing of materials). Materials chosen were C14, C28 and a third related oxygen carrier C13 ($CaMn_{0.8}Mg_{0.2}O_{3-\delta}$).These materials were studied in depth. Performed experiments includes reactivity towards methane and syngas over a large number of cycles at 900°C, 950°C, 1000°C and 1050°C,and their ability to release O_2 at the same temperatures. The following conclusions were drawn based on these in-depth experiments:

- Oxygen carriers based on calcium manganite can release approximately 1 wt% O_2 to the gas phase in the investigated temperature range.
- The reactivity with methane is high, and comparable to that of baseline Ni, with above 90% CH_4 gas yield at temperatures above 950°C for all investigated materials. The amount of solids used corresponded to very low 57 kg/MW.
- The C13 and C14 have higher reactivity with CH_4 compared to C28 at temperatures of 1000°C and below.
- The activity towards methane was found to decrease after testing at 1050°C for C13 and C14, while for C28 there was an increase in reactivity after high temperature testing. In a similar way, the oxygen uncoupling was also found to decrease for C13 and C14, while it remained constant for the C28. It is suggested that the incorporation of Ti can explain the higher reaction stability for the C28.
- The rate of oxygen release was determined and was found to be somewhat greater for C28 compared to C14 and was in the range 0.0003-0.0006 kg O_2/kg OC, s. It is suggested that the reaction with fuel is a combination of CLC and CLOU reactions, with the direct fuel-OC reactions dominating the transfer mechanism at conditions used in this work.
- Full syngas conversion was achieved for all materials utilizing a bed mass corresponding to 178 kg/MW. The very high reactivity with fuel gases, comparable to that of baseline oxygen carriers of NiO clearly makes these perovskite particles highly interesting for commercial CLC application.

In addition to spray-dried particles, a total of 26 different oxygen carrier materials and mixtures with a low NiO fraction were selected and prepared by impregnation. The results with impregnated particles are summarized under the heading WP2.

WP2 Highly reactive material systems with low nickel content

Within WP2, three options were explored to develop oxygen carriers with reduced NiO content, with the aim of maintaining performance in comparison to particles of baseline Ni oxygen carrier.

A. The use of a mixture of low cost materials with a Ni-based oxygen carrier.
B. Develop oxygen carriers containing in the same particle Fe, Mn or Cu and a small fraction of NiO.
C. Improvement NiO utilization in highly reactive materials.

Table 2.1 shows a summary of all the materials prepared by ICB-CSIC, including some characteristics as composition, particle size, crushing strength and XRD data. The Ni-based material taken as reference in this work ($Ni1_{reference}$) was the Ni18-αAl_2O_3, widely used by the ICB-CSIC in the past and developed inside the CLC Gas Power project. A small amount of this material was used for mixing together with particles of other oxygen carriers in order to improve the reforming effect of the final bed material used in the CLC unit. Moreover, the development of Ni-based OC using supports that avoid the interaction with the NiO to form nickel aluminates which decrease the effective use of the Ni inside the particle has been carried out using two preparation routes:

1) impregnation on $MgAl_2O_4$ or $CaAl_2O_4$ supports
2) mixing the metal oxide and the inert material and pelletizing by pressure

Table 2.1. Materials developed at ICB-CSIC.

Sample	Oxygen carrier	Composition (wt. %)	Sintering T (ºC)	Size (μm)	Strength (N)	XRD composition (after calcination)
Ni1 reference	Ni18-αAl_2O_3	18 % NiO αAl_2O_3	950, 1 h	+100-300	4.1	αAl_2O_3, NiO, $NiAl_2O_4$
FeW1	Fe waste	67.4 % Fe_2O_3 21.3 % Al_2O_3 + others	1200, 6 h	+100-300	2.9	βAl_2O_3, Fe_2O_3, SiO_2
Fe1	Fe15-γAl_2O_3	15 % Fe_2O_3 γAl_2O_3	950, 1 h	+100-300	2.5	αAl_2O_3, Fe_2O_3
Fe2	Fe10-αAl_2O_3	10 % Fe_2O_3 αAl_2O_3	950, 1 h	+100-300	2.8	αAl_2O_3, Fe_2O_3
Fe3	Fe15Ni2- γAl_2O_3	14.3 % Fe_2O_3 2 % NiO γAl_2O_3	950, 1 h	+100-300	1.8	αAl_2O_3, Fe_2O_3, $NiFe_2O_4$
Fe4	Fe14Ni5- γAl_2O_3	13.5 % Fe_2O_3 5 % NiO γAl_2O_3	950, 1 h	+100-300	2.0	αAl_2O_3, Fe_2O_3, $NiAl_2O_4$, $NiFe_2O_4$
Fe5	Fe13Ni12- γAl_2O_3	12.7 % Fe_2O_3 5 % NiO γAl_2O_3	950, 1 h	+100-300	2.7	αAl_2O_3, Fe_2O_3, $NiAl_2O_4$, $NiFe_2O_4$
Mn1	Mn30-γAl_2O_3	30 % Mn_3O_4 γAl_2O_3	950, 1 h	+100-300	2.9	αAl_2O_3, Mn_2O_3, Mn_3O_4
Mn2	Mn17-αAl_2O_3	17 % Mn_3O_4 αAl_2O_3	950, 1 h	+100-300	3.5	αAl_2O_3, Mn_2O_3, Mn_3O_4
Mn3	Mn25Ni2.5-γAl_2O_3	25 % Mn_3O_4 2.5% NiO γAl_2O_3	950, 1 h	+100-300	3.2	αAl_2O_3, $MnAl_2O_4$, $NiAl_2O_4$
Mn4	Mn24Ni9-γAl_2O_3	24 % Mn_3O_4 9 % NiO γAl_2O_3	950, 1 h	+100-300	3.0	αAl_2O_3, $MnAl_2O_4$, $NiAl_2O_4$
Cu1 reference	Cu14- γAl_2O_3	14 % CuO γAl_2O_3	850, 1h	+300-500	2.4	γAl_2O_3, $CuAl_2O_4$, CuO(minor)
Cu2	Cu14Ni3- γAl_2O_3	14 % CuO 3 % NiO γAl_2O_3	850, 1h	+300-500	3.1	γAl_2O_3, $CuAl_2O_4$, CuO, $NiAl_2O_4$ (minor)
NiMgAl1 CLCGASPOWER	Ni20-$MgAl_2O_4$	20 % NiO $MgAl_2O_4$	950, 1h	+100-300	4.3	NiO, $MgAl_2O_4$
NiMgAl2	Ni13- $MgAl_2O_4$	13 % NiO $MgAl_2O_4$	950, 1h	+100-300	2.0	MgO, ZrO_2, NiO(minor), $MgAl_2O_4$, $NiAl_2O_4$
NiCaAl4 CLCGASPOWER	Ni11-$CaAl_2O_4$	11 % NiO $CaAl_2O_4$	950, 1h	+100-300	2.4	NiO, $CaAl_2O_4$, $CaAl_4O_7$
NiCaAl5	Ni10-$CaAl_2O_4$	10.5 % NiO $CaAl_2O_4$	950, 1h	+100-300	1.2	NiO, $CaAl_2O_4$, $CaAl_4O_7$
NiCaAl6	Ni20-$CaAl_2O_4$	20 % NiO $CaAl_2O_4$	950, 1h	+100-300	3.5	$CaAl_2O_4$, $NiAl_2O_4$, NiO (minor)
NiCaAl JM	CLC18NPr(1400) Johnson Matthey	21.5 % NiO	n.a.	+100-200	0.5	NiO, $CaO(Al_2O_3)_2$, $CaO(Al_2O_3)_6$

Table 2.2 shows a summary of the materials selected after the TGA characterization and those rejected for further testing in continuous CLC units.

Table 2.2. Summary of the selected and rejected oxygen carriers characterized at ICB-CSIC by TGA.

Sample	**Oxygen carrier**	**Selected for further testing in a continuous CLC unit**	**Comments for rejection**
Ni1 reference	Ni18-αAl_2O_3	Reference Ni-based OC with CH_4 reforming catalytic activity to be mixed with other materials	
FeW1	Fe waste	- To be tested in CLC unit	

		- To be tested in CLC unit by mixing with particles of Ni1	
Fe1	Fe15-γAl_2O_3	- To be tested in CLC unit - To test the effect of S in CLC unit - To be tested in CLC unit by mixing with particles of Ni1	
Fe2	Fe10-αAl_2O_3		Low oxygen transport capacity
Fe3	Fe15Ni2- γAl_2O_3	-To be tested in CLC unit	
Fe4	Fe14Ni5- γAl_2O_3		No advantages with respect Fe3, and higher Ni content
Fe5	Fe13Ni12- γAl_2O_3		No advantages with respect Fe3, and higher Ni content
Mn1	Mn30-γAl_2O_3		Low reactivity
Mn2	Mn17-αAl_2O_3		Low reactivity
Mn3	Mn25Ni2.5-γAl_2O_3		Low reactivity
Mn4	Mn24Ni9-γAl_2O_3		Low reactivity
Cu1 reference	Cu14- γAl_2O_3		Tested in CLC before INNOCUOUS
Cu2	Cu14Ni3- γAl_2O_3	- Tested in CLC unit before INNOCUOUS - To test the effect of S in CLC unit.	
NiMgAl1 CLCGASPOWER	Ni20-$MgAl_2O_4$		Tested previously to INNOCUOUS.
NiMgAl2	Ni13- $MgAl_2O_4$		Low reactivity
NiCaAl4 CLCGASPOWER	Ni11-$CaAl_2O_4$		Tested previously to INNOCUOUS.
NiCaAl5	Ni10-$CaAl_2O_4$	-To be tested in CLC unit	
NiCaAl6	Ni20-$CaAl_2O_4$		Low Ni utilization
NiCaAl JM	CLC18NPr(1400) Johnson Matthey		Low crushing strengh

Different mixtures of oxygen carrier particles or low cost materials containing metal oxides and a low NiO fraction potentially active for gas CLC have been evaluated in the continuous CLC unit to obtain oxygen carriers with reduced NiO. In Deliverable 2.2 some mixtures of oxygen carriers were selected for testing in the continuous CLC unit. Table 2.3 shows a summary of these materials. Two of the materials (FeW1 and Fe1) were tested by separate and mixed with small amounts of the Ni-based oxygen carrier Ni1 to analyze the possible advantage of the CH_4 reforming catalytic effect of this addition (Series 1-2). Considering the promising results obtained with the impregnated Fe-based materials, characterized by a high reactivity and oxygen transport capacity, special emphasis in the development of this type of particles was applied. Thus, the effect of the presence of sulphur in the fuel gas was also tested with the particles Fe1 in continuous operation (Series 3). Moreover, materials containing Ni and other metal oxide in the same particle were evaluated (Series 4-5). The mixed oxide Fe3 (Fe15Ni2- γAl_2O_3) was tested in the CLC unit. The comparison of the results obtained with this oxygen carrier and those obtained with the mixture of particles Fe1+Ni1, made it possible to determine whether a mixture of particles or a composite particle containing Ni is the best route for utilizing the catalytic activity of Ni.. The effect of sulphur was tested in the particles Cu2 (Cu14Ni3-γAl_2O_3), in order to complete the characterization of this material for its use in CLC. Finally, a Ni-based oxygen carrier based on resistant and inert support, NiCaAl5, was also tested (Series 6). Also in the table it is shown what has been evaluated in the continuous unit and the deliverable in which the results has been presented.

Table 2.3. Materials tested in the continuous unit.

Series	Bed material	Oxygen carrier 1	Oxygen carrier 2	Evaluation in 500 W CLC unit	Deliverable
1	FeW1 + Ni1 $_{reference}$	Fe waste	Ni18-αAl2O3	Effect of Ni addition	D.2.3
2	Fe1 + Ni1 reference	Fe15-γAl_2O_3	Ni18-αAl_2O_3	Effect of Ni addition	D.2.3
3	Fe1	Fe15-γAl_2O_3	-	Effect of S	D.2.3

4	Fe3	Fe15Ni2- γAl_2O_3	-	Effect of Ni addition	D.2.4
5	Cu2	Cu14Ni3- γAl_2O_3	-	Effect of S	D.2.4
6	NiCaAl5	Ni10-$CaAl_2O_4$	-	Effect of support	D.2.3

The continuous evaluation of the materials has shown different results. The oxygen carrier coming from a waste material, FeW1, needed an addition of 5 wt.% NiO to reach high combustion efficiencies, reaching near full combustion at oxygen carrier to fuel ratios higher than 3 with bed inventories of 1900 kg/MW_{th}. When the addition of NiO was made to a synthetic Fe-based oxygen carrier, Fe1, the effect was only relevant at low temperatures (830°C). At higher temperatures (880°C), the solids inventory necessary to reach full conversion of methane was around 500 kg/MWth which corresponds to a Fe inventory of 50 kg/MW_{th}. The effect of the presence of sulphur in the fuel gas and the attrition behaviour during continuous long term operation was also analysed with this material. The presence of H_2S in the fuel gas does not affect the combustion efficiency, independently of the amount of S in the gas stream. Working at optimum conditions ($\phi > 1.5$), the small amount of SO_2 released from the AR fulfil legislation about gaseous emissions. Most of the sulphur fed with the fuel gas is released as SO_2 in the flue gas from the FR affecting only to the quality of the CO_2 produced. The results obtained showed that synthetic Fe-based oxygen carrier developed in this work was highly reactive and sulphur resistant and, consequently is a suitable material to be used in a CLC process using gaseous fuels containing H_2S. However some improvements in the properties of this material are needed regarding the attrition behaviour and the stabilization of the oxygen transport capacity of the material.

Two combined mixed oxides OC materials of Cu-Ni and Fe-Ni were prepared and tested in the 500W CLC unit. No substantial improvement of the combustion efficiency were reached working with material Fe3, containing iron and nickel oxides impregnated over the same alumina particle respect to the results obtained with the Fe-based oxygen carrier without mixing, Fe1. The material, Cu2, Cu14Ni3-γAl_2O_3 was developed previously and contains 3 wt.% of NiO which is present as $NiAl_2O_4$ and improves the attrition resistance at high temperatures. The combustion efficiency of the Cu2 material was investigated using CH_4 containing H_2S. It was found that main part of S was in the FR outlet as SO_2 and only small concentrations (<10 vppm) were present in the AR outlet. At high operating temperatures (850-880°C) combustion efficiency was maintained with time and no loss of carrier reactivity was observed although some S accumulation on the carrier was needed to close the S balance. However, at low temperatures (800 °C) there was a deactivation of the OC and unconverted CH_4 appears at FR outlet. Therefore, Cu1 material, a carrier with only CuO, has better behaviour regarding S in the feed.

The Ni-based oxygen carrier, NiCaAl5, developed inside this project, using a resistant support which avoids the NiO-support interaction, was tested in the continuous unit. This material showed very good performance for CH_4 combustion with near complete combustion at oxygen carrier to fuel ratios ranging 1.0-1.2. A solids inventory in the fuel reactor of 180 kg/MWth was necessary to reach a combustion efficiency of 99 % which corresponds to 15 kg of Ni metal.

As a summary, Table 2.4 shows the performance of the different impregnated oxygen carriers for CH_4 combustion with respect to the Go/No-Go criteria of the INNOCOUS project. According with these criteria, Ni10-$CaAl_2O_4$ material does not meet the criteria of Ni< 5% content, although this material contains the lowest amount of metallic Ni (15 kg/MW_{th}) of all Ni-based carriers developed worldwide. The materials Fe15-γAl_2O_3, Fe15Ni2-γAl_2O_3 and Cu14Ni3-γAl_2O_3 fulfill all the criteria. The impregnated carrier Fe15-γ Al_2O_3 showed similar performance to Ni18-α Al_2O_3 (reference) and Cu14-γ Al_2O_3 (reference). But this oxygen carrier is a non-toxic material (0 wt.% Ni content) and cheaper than those previously developed by impregnation.

Table 2.4. Results of impregnated OC testing in 500 W_{th} continuous CLC unit with respect to Go/No-Go criteria.

Oxygen carrier	FR Inventory	Fluidizability &	Attrition	Operation	CS >1	Reduction in
Ni18-αAl_2O_3 $_{(reference)}$	600	OK	0.01	250	OK	14
Cu14-γAl_2O_3 $_{(reference)}$	390	OK	0.04[a]	650	OK	0
Cu14Ni3- γAl_2O_3	260	OK	0.04	45	OK	2.3
Fe15Ni2-γAl_2O_3	870	OK	-	21	OK	1.6
Fe15-γAl_2O_3	500	OK	0.08	85	OK	0

*measured in a 500 W_{th} CLC unit at 900°C, [a] measured in a 10 kW CLC unit at 800°C

WP3 Innovative development of scale up ready particle preparation routes

This Work Package involves the assessment of existing and innovative approaches for oxygen carrier preparation and manufacturing scale-up, together with pilot-scale delivery of both spray dried and impregnated particles (> 100 kg batch-size) for testing in the CLC 120 kW_{th} pilot-unit at TUV.

The prior experience of Chalmers, CSIC and VITO with oxygen carrier preparation, using freeze granulation, spray drying and impregnation techniques was inventorized by VITO, with input from Chalmers and CSIC. This inventory of recipes for oxygen carrier preparation via different preparation routes (Task 3.1, Deliverable D3.1), has formed the basis for the further development of scale-up ready manufacture processes. Production methods suited for large scale particle preparation, such as impregnation and spray drying - well established industrial methods for production of dry solid particles in large quantities - are considered suitable for oxygen carrier production.

The preparation of suspensions, spray drying and subsequent processing has been performed by VITO for small and medium-size batches prior to Task 3.3. JM has also input expertise on scale up where appropriate. The product specifications in terms of particle size, particle size distribution, bulk and particle density, friability, activity, have an impact on the overall manufacture process of the oxygen carrier material. As is shown in the Deliverable D3.4, this is not only related to the spray drying step itself, but to the whole production chain, which encompasses several processing steps. In this deliverable, fulfilling Task 3.2, the impact of several process steps, such as composition, nozzle diameter, pore former addition, milling time, sieving, and sintering treatment is discussed in detail. Some key points from the task are as follows:

- VITO was able to successfully synthesize all >60 different compositions in the right size distribution, by tuning the process parameters such as slurry composition (solids loading, binder content, milling time) and adapting sieving process to the specific shrinkage of the particles. For testing at Chalmers, 1 kg batches of 100-200 µm fraction were prepared, of which 100 g was sintered at the specified temperature.
- The effect of the nozzle size on the overall spray drying process yield can be quite large, with differences of almost 10% in yield. A 2.0 mm nozzle opening was selected for the screening of the compositions. This optimal nozzle size was chosen for the production of the large batches. It has to be noted that the nozzle size should be tested and optimized for each (slurry) composition.
- Options to increase porosity while maintaining sufficient mechanical strength were explored, by adding pore formers to the oxygen carrier slurry which is spray dried. When using graphite as a pore former, particles with sufficient strength can be obtained using up to 15 wt% pore former in the oxygen carrier manufacture.
- The mechanical properties of the different granules do not vary significantly with milling time for the selected compositions in the selected conditions.
- The effect of the sintering step was also assessed for selected compositions. The trend of increasing strength with sintering temperature is not linear, and dependent upon composition. Increasing the time of the sintering treatment at a specific sintering temperature also increases the strength of the oxygen carrier particles, along a linear trend, but dependent upon composition.

Clearly, by careful manipulation of the process parameters, the properties of the final product can be tuned towards application in CFB CLC. This makes spray drying a very versatile and suitable manufacturing process for production of oxygen carriers at the industrial scale.

Based on the selection of the composition of the material (D1.3, MS3 and MS7), and the optimization of the fundamentals of the spray drying manufacturing route (D3.4), two large (>100 kg) batches of spray dried oxygen carrier have been manufactured successfully, i.e. C14 and C28, as part of Task 3.3. Quality of the batch was continuously monitored during the production. These large batches have been shipped to partners (TUV, Chalmers, CSIC) in various quantities for testing in their CLC installations. Completion of this scale-up activity satisfies two Deliverables and associated Milestones for WP3, namely D3.5, MS4 and D3.6, MS9.

As already indicated, for manufacturing scale-up the established processes of spray drying and impregnation have been further assessed in this WP. With respect to impregnation, a batch of 15 kg of an oxygen carrier comprising 19.5 wt.% NiO supported on gamma-Al2O3 (100-300 µm) was prepared using a dry impregnation method by CSIC (Task 3.4, Deliverable D3.2). The preparation method, characterisation (crushing strength, porosity, particle density, B.E.T surface area, XRD) and initial reactivity testing (TGA) were established. This batch of oxygen carrier was used for testing in the 120 kWth unit at TUV, in combination with natural minerals (ilmenite) as part of WP4. This also satisfies the associated Milestone, MS1. Part-way through the project, supported by a preliminary investigation on EHS issues associated with the future application of Ni-based oxygen carriers, especially within the EU, it was decided to focus the efforts towards developing a non-nickel material for scale-up activities. For this purpose, CSIC and the Consortium selected a nominal 15 wt.% Fe2O3 supported on gamma-alumina oxygen carrier, as used in WP2 that had proven to perform well in CSIC's 500 kWth unit. A scaled-up batch, based on this impregnated material and associated recipe was produced by JM, utilising the same lab-grade raw materials. In addition to an initial 10 kg trial batch send for initial testing at CSIC (TGA, 500 Wth CLC, characterisation), two 70 kg batches of differing particle size ranges (100-300 µm and 300-500 µm) were produced and shipped to TUV for pilot-scale testing. Different particle size ranges were selected to allow for some investigation of the importance of this parameter in the pilot-CLC unit. It was observed that the scaled-up impregnated batches exhibited a high attrition loss, especially at the start of the experimental runs, thought due to a higher concentration of Fe2O3 content on and towards the surface of the particles, rather than a more homogeneously spread distribution of the active species in the pores of the alumina support. This discrepancy is envisaged to be rectifiable for scale-up production, but does highlight the non-trivial nature of taking a lab-prepared material and producing it at a larger scale, whilst still maintaining its performance properties. Production of the scaled-up batch and subsequent shipment to TUV constituted Deliverable D3.3 and the associated Milestone, MS10.

JM has conducted air-jet attrition tests (based on ASTM D5757) of several impregnated and spray dried particles produced within the project, as reported in the project's Mid-term Report. Although deemed a useful tool for initial assessment of mechanical strength of the oxygen carrier particle, it does not account for high temperature effects and chemical-attrition due to the morphology changes of the particle during multiple redox cycles. Further work developing an appropriate test protocol for mechanical strength (attrition) needs to be developed in future projects.

Task 3.5 - Technical and economic assessment of the scaled-up particle production has been addressed. The purpose of this task is to use the lab-scale processes developed in Tasks 3.3 and 3.4 as the basis of an initial assessment on the viability of manufacturing these materials at commercial scale at a European location. Four exemplary oxygen carrier formulations where assumed, two made via a spray drying route ("C14" from WP1 and also Ni-based "VITO-b", from previous "CLC Gas Power" project, as a reference) and two by impregnation (Fe2O3/Al2O3 and CuO/Al2O3 from WP2). A 800 te/yr scale of manufacturing facility was selected for the costing exercise as this may represent a commercial-scale.

The following points summarise the JM oxygen carrier "manufacturability" study for Deliverable D3.7:

- In general terms the lab-scale production routes are relevant to those used widely in the solids processing industries and there does not appear to be any significant technical barriers in the manufacturing process.
- Certain of the support materials (and dispersants) used for the original lab-scale recipes are not available in the tonnages required at the industrial scale. (Budget quotations for alternative materials were sought for use in quantification of the variable costs in D3.8).
- Containment of nickel oxide (such as for "VITO-b") and other toxic materials is a critical aspect in the design of oxygen carrier manufacturing facilities. In the preparation of this report no technical or economic barriers have been identified to providing the correct level of containment to meet the current occupational exposure limits in force in the EU. Should tighter regulatory limits be introduced (e.g. in line with those in the pharmaceutical industry), the cost implications for the manufacturability of Ni-based carriers would be considerable.
- Ultimately the product specification and performance requirements will determine the manufacturing route more than cost per se, and it is expected that certain carriers will be suited to impregnation routes and others to a spray drying route. The choice will also be influenced by considerations not accounted for in the present study, including the product yield (more important for high raw material cost particles such as Ni), and whether fines can and need to be recirculated in order to improve the product yield.

The scale of production of oxygen carriers to-date has been in the low kg range and has used lab-scale raw materials. This presents two key challenges to be addressed in scale up:

- Identification of economic, commercial-scale raw materials which enable manufacture of an oxygen carrier of the correct specification.
- Further development of the manufacturing route and scale-up to, and demonstration of production at a scale which is representative of a commercial-scale process. To achieve this it is necessary to well-understand which critical physical and chemical characteristics of the product define its performance and to maintain these within a defined range during the scale-up and manufacturing operations.

In Deliverable D3.8, capital estimates have been prepared using the Process Flow Diagrams (PFD) developed as part of the 'Manufacturability Summary' report (D3.7). On looking at the manufacturing cost data, one could interpret that spray drying is the less expensive process, but based on the level of analysis conducted that would be misleading. A direct comparison of spray-drying vs. impregnation for a specific carrier formulation/composition has not yet been conducted, as lab-studies are still needed to confirm the relative performance of equivalent routes. Therefore, at this stage of the analysis it can be stated that no manufacturing route stands-out as being preferential for oxygen carrier production. Additionally, the CAPEX of the impregnation route may be decreased if the desired active metal loading was less and/or could be achieved in one single impregnation step (certainly thought possible for the Cu-based material at least). Furthermore, another possible option, co-precipitation, which may offer manufacturing cost and performance benefits for OC's with high-metal loading, mixed component compositions, has not yet been similarly evaluated.

A partial fixed and variable manufacturing costs assessment has been carried out for representative oxygen carrier formulations. It is revealed that generally the raw materials themselves constitute a significant part of the manufacturing cost and thus a strategy to optimise the cost would first focus on the nature and supply of the raw materials (a prerequisite being that new material options would need to be technically proven at lab-scale). As a result of this exercise some Projected Market Prices have been generated as an indicative guide as to what a vendor may charge for supply of manufactured (first generation) oxygen carrier products. This pricing information was used in WP5 for Task 5.3, D5.3. The indicative costing information, together with assumptions, is contained in D3.8.

For Deliverable D3.9, It was deemed not viable to conduct a benchmarking exercise per se of the manufacturing route at this stage, with no recommended standard manufacturing process yet identified (based on information borne-out of INNOCUOUS to-date, together with that from previous CLC-based EU projects and the open literature). Instead D3.9 consolidated D3.7 and D3.8 and provided some recommendations for further work:

In order to attempt to rank manufacturing routes for oxygen carrier production and create a benchmark process of sorts, the following tasks need to be performed:

- A technical and economic assessment for the manufacture at multi-tonnage scale by different routes of one or more exemplary fixed oxygen carrier formulations/compositions.
  - Using industrially-relevant raw materials and with product specifications.
  - Inclusion of a co-precipitation manufacturing route in the assessment.
  - Note, as mentioned previously, for some oxygen carrier compositions certain manufacturing routes may not be suitable from the outset.
- For the different routes, to include an assessment of the impact of recycling of out-of-specification material produced during manufacture to improve finished product yield. Also, the potential of reprocessing (to new carriers) discharged/spent oxygen carriers from the CLC reactor unit should be evaluated.

WP4 Testing of new particles under relevant conditions

4.1 Testing of oxygen carrier materials in 300 W CLC unit

During the project, ten different spray-dried oxygen carrier identified as promising in WP1 have been examined in Chalmers 300 W reactor unit. The materials have been examined both with respect to their capability to oxidize natural gas (CLC), and with respect to their capability to release gas phase oxygen during fluidization with inert gas (CLOU). A list of examined materials can be found in Table 4.1.

Table 4.1 Summation of the fuel operation in Chalmers 300 W reactor unit.

Sample	***Material composition***	***Fuel operation***	***Maximum Fuel***	***Rate of***
C13	$CaMn_{0.8}Mg_{0.2}O_{3-\delta}$	15[1]	100	Low
C14	$CaMn_{0.9}Mg_{0.1}O_{3-\delta}$	16[1]	100	Low
C28	$CaMn_{0.775}Mg_{0.1}Ti_{0.125}O_{3-\delta}$	40	100	Low
M1	$MnMgO_3$	2[2]	93	Moderate
Cu1_950	40 wt% CuO on ZrO_2	2[3]	100	Large
Cu1_1030	40 wt% CuO on ZrO_2	5[3]	100	Large
Cu5	40 wt% CuO on CeO_2	5[3]	100	Large
Cu14	40 wt% CuO on Y-ZrO_2	11[3]	100	Large
MS1	$Fe_{0.66}Mn_{1.33}SiO_3$	7[3]	100	Large
MS2	$FeMnSiO_3$	15[3]	85	Large
F13	$Fe_{0.5}Mn_{0.5}TiO_3$	12	80	Moderate

**Low = less than 0.05wt%/h in filters, moderate = 0.05-0.5 wt%/h, large = more than 0.5 wt%/h.*

[1] Experiments aborted due to mechanical failure of reactor.

[2] Experiments aborted due to particle agglomeration.

[3] Experiments aborted due to severe attrition and loss of solids circulation.

As can be seen in Table 4.1, a majority of the materials showed full fuel conversion also in the 300W reactor. All manganese-based materials were quite dependant on temperature and in order to achieve complete conversion about 950°C was required, see figure 4.6 for an example. In contrast, copper based materials worked well with respect to fuel conversion also at lower temperatures. All materials in Table 4.1 also released gas phase oxygen at relevant conditions.

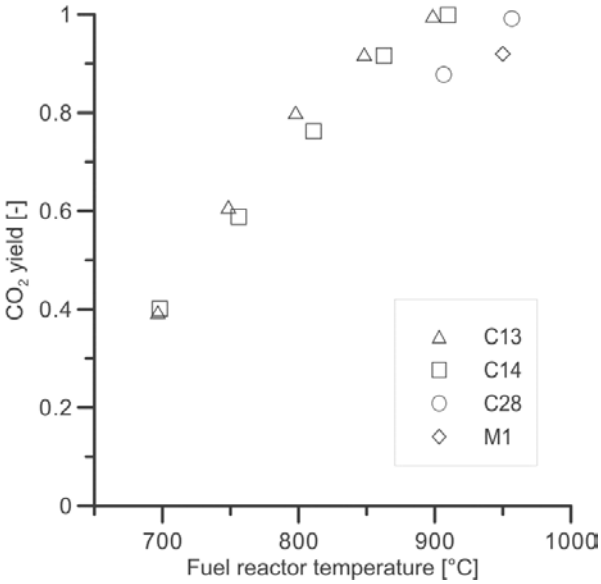

Figure 4.1. Fuel conversion (CO_2 yield) as a function of temperature for C13, C14, C28 and M1 in 300W reactor. The air flow was 6 L_N/min for C13, C14 and C28 and 7 L_N/min for M1. The fuel flow was 0.3 L_N/min for C13, C14 and M1 and 0.4 L_N/min for C28.

Unfortunately, several of the examined materials showed quite poor mechanical or chemical stability, i.e. had a rather large or even very large rate of particle attrition during operation. The CaMnO3-based materials performed very well in all aspects though. Hence, based on these experiments, C14 and C28 was chosen for up-scaling and further experiments in 10 kW at Chalmers and 120 kW reactor at TUV. A detailed description of the 300W reactor experiments can be found in deliverable D4.3.

4.2 Long-term testing of oxygen carrier materials in 10 kW CLC unit

Based on the experiments in the 300 W reactor the oxygen carrier materials C14 and C28 were produced in new batches of 25 kg each and used to perform additional experiments in Chalmers 10 kW reactor. This reactor involves gas velocities relevant for comparison to large-scale units, i.e. around 3 m/s in the riser, 8 m/s in the cyclone inlet and 20 m/s from air inlet nozzles. Because of this, experiments performed in this reactor should give a much better idea about the performance of oxygen carrier materials during real-world conditions. C14 was operated for 55 h with natural gas combustion and C28 was operated for 100 h, also with natural gas.

Both materials gave very high conversion of the fuel and had low rate of attrition. It was also shown that very low concentrations of methane, carbon monoxide and oxygen at the outlet of the fuel reactor could be obtained simultaneously with both of the materials. Both C14 and C28 were capable of providing full conversion of fuel at certain conditions. Temperature, rate of solids circulation and air ratio was identified as important factors to achieve high fuel conversion. See figure 4.2 for an example.

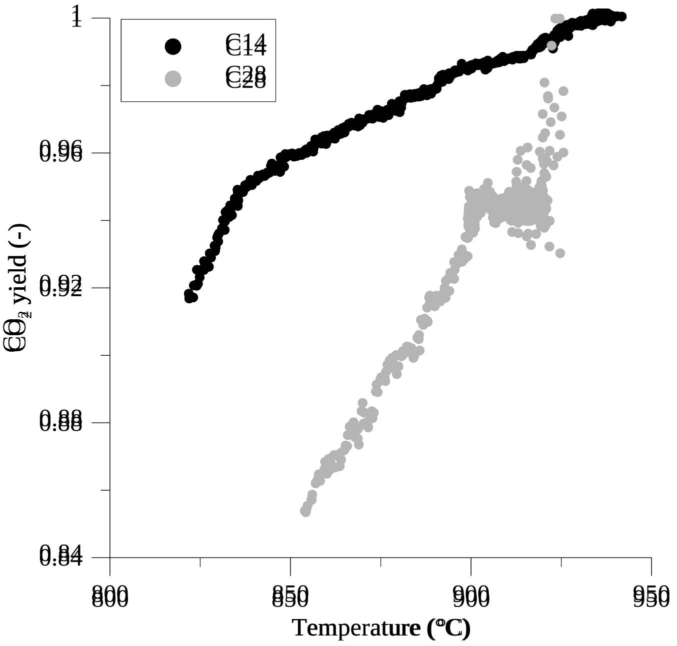

Figure 4.2. Fuel conversion (CO_2 yield) as a function of fuel reactor temperature for C14 and C28 in 10 kW reactor. The air flow was set to *200 L_N/min and the fuel flow to 9 L_N/min for C14 and the air flow to 160 L_N/min and the fuel flow to 7 L_N/min for C28.*

Both C14 and C28 were found to have very good resistance towards attrition, even though C28 provided quite a lot of fines during the first few hours of operation. From the measured fraction of fines in the elutriated material during the operation in the 10 kW reactor it was concluded that both C14 and C28 can withstand longer continuous operation. An approximate life time of 12 000 h for C14 and an approximate life time of 9 000 h for C28 were estimated. A detailed description of the 10 kW reactor experiments can be found in deliverable D4.3.

4.3 Parameter study of oxygen carrier materials in 120kW CLC unit

Overview on parameters used to describe the oxygen carrier materials

The 120kW unit at TUV allows different variations of process parameters to characterise the CLC process, also with focus on different oxygen carrier materials. These parameters are:

- *Inventory:* The inventory of solids influences the gas – solid contact time in both reactors. Increasing the inventory also increases the solids circulation between the reactors. The active solid inventory ($m_{solid, act}$) is derived from the pressure drop over the fluidized beds of the air reactor and the fuel reactor and is used to show the variation of the total inventory. Using the active inventory of the fuel reactor and relating it to the fuel power, a specific reactor inventory per fuel power can be derived. It gives the mass of oxygen carrier per megawatt.
- *Air to fuel ratio:* The air to fuel ratio gives the relation of the stoichiometric demand of oxygen for full combustion of the fuel with the oxygen supplied in the air reactor. Using oxygen carriers with low fuel conversion, it is necessary to feed additional fuel to the air reactor (in this case propane). Since this additional fuel lowers the amount of available oxygen in the air reactor, the effective air to fuel ratio (λ_{eff}) is used to describe the oxygen supply in the air reactor. This value takes the air demand of the additional fuel into account.

- *Fuel power:* The amount of fuel influences both, the fuel reactor and the air reactor. Increasing the power leads to a more turbulent bed in the fuel reactor and with a constant air to fuel ratio the amount of air in the air reactor has to increase. This leads to a higher global solids circulation rate.
- *Fuel reactor temperature:* It is not possible to set the temperature in the air reactor and the fuel reactor at the same time. Solids circulation, conversion and fuel power cause a corresponding temperature in the second reactor. In this study the fuel reactor temperature has been chosen as characteristic value to show the temperature dependency of the different oxygen carriers.
- *Oxygen carrier to fuel ratio:* This parameter is not accessible during the experiments, but it is useful during evaluation of the results and to compare different oxygen carrier materials. It correlates the amount of available oxygen from the oxygen carrier transported to the fuel reactor with the oxygen demand of the fuel fed to the fuel reactor. This value depends on the global solids circulation rate, the degree of oxidation of the particles leaving the air reactor and the fuel power.
-

Table 4.2 gives an overview of the operating range of all experiments for the above described parameters. The inventory for the mixed oxides is not shown in this table, since in this series the amount of Ni – catalyst has been varied and not the total inventory.

Table 4.2: Overview of operating conditions

	$m_{solid, act}$	λ_{eff}	P_{fuel_FR}	ϑ_{FR}	Operating points	Fuel		
	[kg]	[-]	[kW]	[°C]		n.g.	Propane	Syngas
Mixed oxides	-	0.5 - 1.2	60 - 130	910 - 970	56	x	-	x
C14	18 - 74	1.2 - 2.0	50 - 120	900 - 960	40	x	x	-
C28	12 - 30	1.1 - 1.9	50 - 100	950 - 960	35	x	x	-
$Fe17_{small}$	19 - 27	1.3 - 3.2	40 - 100	940 - 950	32	x	x	-
$Fe17_{large}$	17 - 58	1.5 - 3.7	40 - 90	890 - 970	20	x	-	x

Mixed oxide testing

The aim of this experimental study was to quantify the influence on fuel conversion performance of a highly active reforming catalyst in addition to a natural iron-based bulk oxygen carrier at the 120kW CLC pilot plant. For the experiments, a mixture of the mineral ilmenite and artificial Ni-19γ-Al_2O_3 particles was chosen as oxygen carriers. Ilmenite was chosen because of its capability to react with CO and H_2 as well as its abundance and low price. Ni-19γ-Al_2O_3 has been verified in other experiments as a promising reforming catalyst. This inspired the idea of a synergy effect between the two mixture components which could lead to a complete conversion of CH_4. It was assumed that this could be achieved already at low Ni-19γ-Al_2O_3 mass fractions thus obtaining a cost effective yet highly performing oxygen carrier which could make the CLC technology competitive.

In order to verify this, experiments were planned in order to investigate the influence of increasing Ni-19γ-Al_2O_3 concentration and other parameters on the overall CH_4 conversion. Six experiments were conducted, whereby the mass fraction of Ni-19γ-Al_2O_3 was increased from 0 to about 16 wt. %. In total, 56 operating points corresponding to 13 mixtures were investigated. The total solids inventory mass was kept close to 85 kg.

As a result of the experimental campaigns it turned out that the CH_4 conversion was not as high as expected, but increased only gradually with catalyst addition from 40% to 50% (Figure 4.3). This was also observed during the additional experiment with up to 33 kg of Ni-19γ-Al_2O_3 in the 85 kg mixture. For syngas (1:1 CO:H_2) the CO conversion even decreased with addition of catalyst, proving a higher reactivity of ilmenite for CO conversion compared to Ni-19γ-Al_2O_3. The H_2 conversion stayed about constant. Several reasons may contribute to the low conversion efficiency and the low effect of the catalyst in the investigated conditions. The most probable explanation is that Ni-19γ-Al_2O_3 as $NiAl_2O_4$ (nickel spinel) is so stable even under the conditions in the fuel reactor that no metallic Ni is formed which would be necessary for a fast reforming reaction of CH_4. The presence of NiO as Ni-19γ-Al_2O_3 exhibits slow reduction kinetics compared to the low mean residence time in the reactor. Locally, in the emulsion phase of the fluidized bed, there may be lower CO/CO_2 and H_2/H_2O ratios because of the presence of Fe_2O_3/Fe_3O_4 and $Fe_2TiO_5/FeTiO_3$, leading to a competition for the CO and H_2 respectively. The low reforming activity of non-reduced catalyst leads to the observed low conversion of CH_4. The thermodynamic explanation is supported by Figure 4.4.

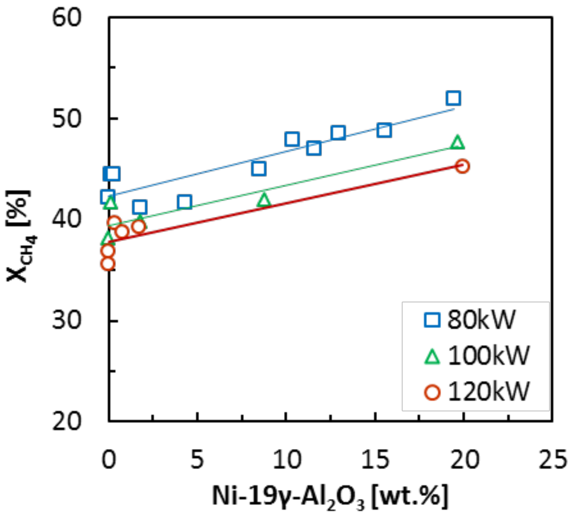

Figure 4.3: Methane conversion in the 120 kW pilot plant at 960°C in the fuel reactor dependent on fuel power and catalyst concentration in the oxygen carrier mixture.

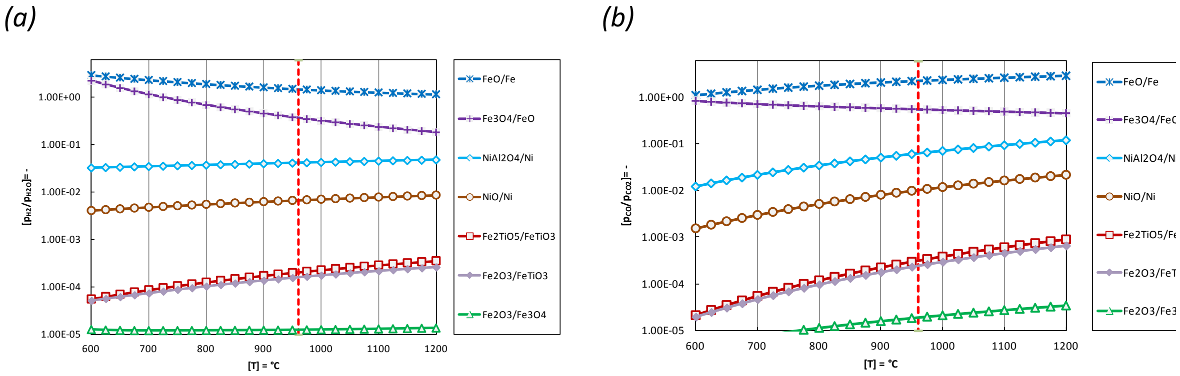

Figure 4.4: Thermodynamic equilibrium partial pressure ratios of H_2/H_2O (a) and CO/CO_2 (b) for the reduction/oxidation pairs possibly present in the investigated mixed oxide system.

Using an inventory of 85 kg and an average fuel power of more than 100 kW leads to an estimated inventory/fuel power relation of about 1 t/MW_{th} (whereas the best Ni-based oxygen carriers have an inventory of 25-50 kg/MW_{th}). Also a relatively high attrition rate of ilmenite of 3-4 kg/h was observed. Using the same reactor dimensions (diameter/height, etc.) and fluid properties this would mean an attrition rate of 30-40 kg/MWh_{th}.

It can be concluded that the mixed oxides consisting of ilmenite/ Ni-19γ-Al_2O_3 did not fulfil the expectations and are not a suitable oxygen carrier system for practical application.

A general conclusion is that catalysts which exhibit highest steam reforming reactivity at fully reduced conditions are not necessarily suitable as rate promoters in mixed oxide CLC.

Testing of non – nickel oxygen carrier systems

In this second experimental study of the project the oxygen carriers developed in WP3 have been tested under relevant conditions in the 120kW CLC unit at TUV. The oxygen carrier materials investigated were: Fe17 (a Fe – based oxygen carrier, made by impregnation), C14 and C28 (both spray dried materials based on $CaMnO_3$ perovskite structure and both with CLOU capabilities).

The conditions for the parameter variation during the different experiments are already described above. The following sections only deal with the results of the experiments.

Results of the Fe17 – testing:

Two Fe – based oxygen carrier materials with different size ranges have been investigated. The use of Al_2O_3 as support material makes the Fe^{2+}/Fe^{3+} redox system accessible. Experiments have shown that the particles leaving the air reactor are always fully oxidized. That means that the oxidation of the oxygen carrier is not limiting. The fuel conversion was lower in the 120kW unit than CSIC reported. A fuel conversion of 60% was the best result obtained as shown in Figure 4.5. The amount of partially converted fuel (CO and H_2) was low. Increasing fuel conversion could be observed with increasing oxygen availability in the fuel reactor, with increasing oxygen carrier to fuel ratio (Figure 4.5 a). Increasing the gas solid contact time with higher specific solid inventory in the fuel reactor allows better fuel conversion (Figure 4.5 b). Analysis of the particles after the experiments showed a significant loss of the active oxygen carrier material, but the loss of iron stabilized after several hours of operation. The particle attrition rate did not decrease, attrition occurred during the whole period of oxygen carrier testing.

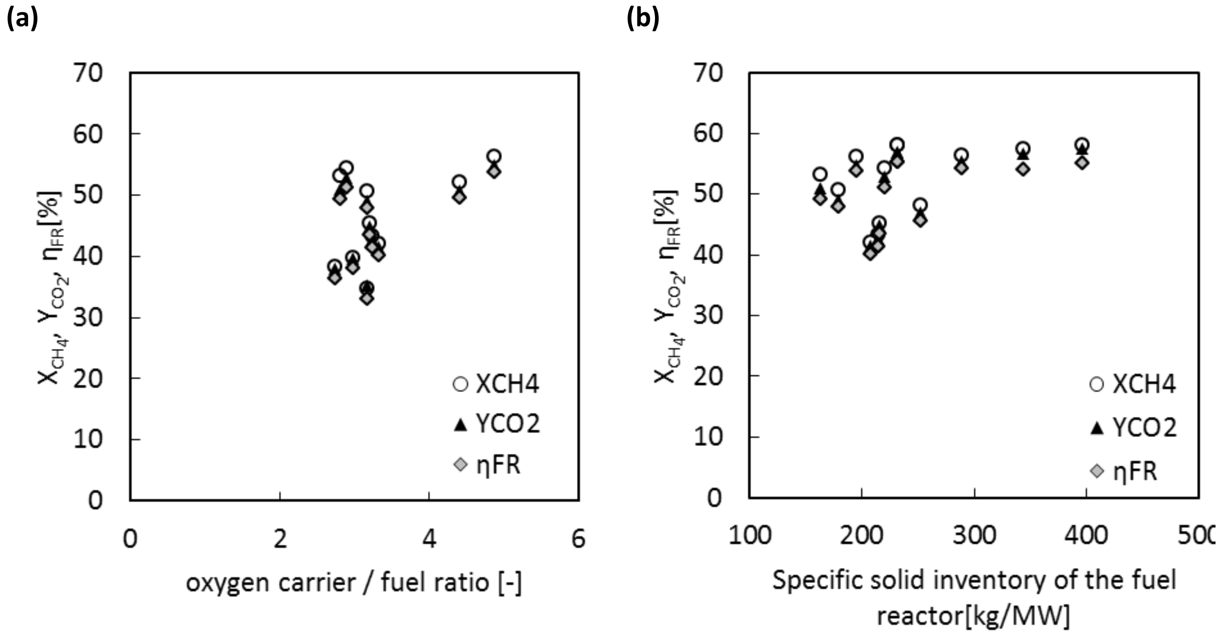

Figure 4.5: Main results of the test runs using the Fe17 material. (a) Effect of the oxygen carrier to fuel ratio on the fuel conversion, (b) Effect of the specific fuel reactor inventory

Results of the C14 – testing:

The C14 oxygen carrier material has been tested in four experiments. That gave about 40 hours of CLC operation. With this oxygen carrier stable operation was possible. Experiments have shown that higher temperatures give better conversion. During one experiment the air in the air reactor has been diluted with nitrogen to lower the oxygen concentration but the total amount of fluidizing gas was constant to allow comparable solids circulation rates. This investigation showed that lowering the oxygen concentration in the air reactor also lowers the fuel conversion in the fuel reactor. Increasing the solids circulation rate and high oxygen concentrations in the air reactor, which means increasing the oxygen carrier to fuel ratio, allowed full fuel conversion, compare Figure 4.6a. Also a higher specific inventory in the fuel reactor caused better fuel conversion (Figure 4.6b). With a specific inventory of about 350kg/MW in the fuel reactor full fuel conversion was possible. For operating conditions with incomplete fuel conversion also a little amounts of carbon monoxide and hydrogen were present in the fuel reactor off gas. Under operating conditions with full methane conversion no carbon monoxide was present, though. Oxygen in the fuel reactor off gas was noticeable for operating conditions with good fuel conversion (above 95%) but was at the lower end of the detection limit of the oxygen analyser. Only for operating conditions with full fuel conversion excess oxygen was significantly present in the fuel reactor off gas stream (up to 0.4vol.%wet basis).

In the first period of the testing the attrition rate was quite high, about 1kg/h. After some hours of operation it decreased and stabilized at a moderate value of about 0.6kg/h.

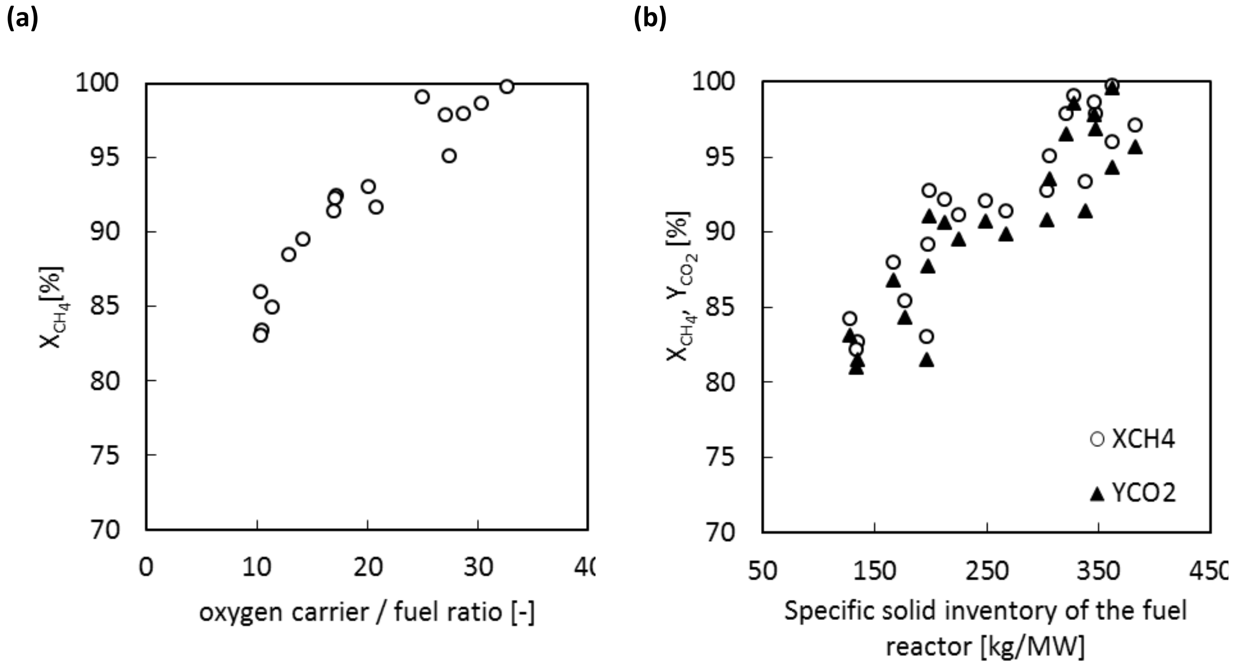

Figure 1.6: Main results of obtained from the test runs using C14 as oxygen carrier. (a) Influence of the oxygen carrier to fuel ratio on the methane conversion and on the CO_2 – yield, (b) Influence of the specific fuel reactor inventory on the fuel conversion.

Results of the C28 – testing:

With the C28 oxygen carrier material 3 experiments have been carried out. The experimental procedure was similar to the C14 testing to be able to compare these two quite similar oxygen carrier materials more easily. The C28 showed a high attrition rate at the beginning of the experiments. It was even higher than for the C14. The attrition rate during the first hours of the first experiment was about 1.5kg/h. The attrition rate decreased with time but was higher than for the C14 material. Attrition of the used C28 oxygen carrier was about 1kg/h.

The temperature dependency was quite similar to the C14 material. High temperatures caused better fuel conversion. The reduction of the oxygen content in the air reactor showed a decrease of the reactivity in the fuel reactor. The material behaved similar to the C14 oxygen carrier. Increasing the solids circulation rate and as a consequence the oxygen carrier to fuel ratio led to full fuel conversion in the fuel reactor (Figure 4.7a). Compared to the C14 results almost no partially converted fuel (carbon monoxide and hydrogen) was present in the fuel reactor off gas. Also for operating conditions with low fuel conversion partial fuel conversion did not occur. Oxygen in the fuel reactor off gas was noticeable for operating conditions with good fuel conversion (above 95%) but was at the lower end of the detection limit of the oxygen analyser. A significant increase, like observed with the C14 material, did not occur with the C28 oxygen carrier. The specific inventory to reach full fuel conversion was also in the same range like for C14. About 320kg/MW of oxygen carrier in the fuel reactor are necessary to fully convert the fuel in the 120kW pilot unit, compare Figure 4.7b.

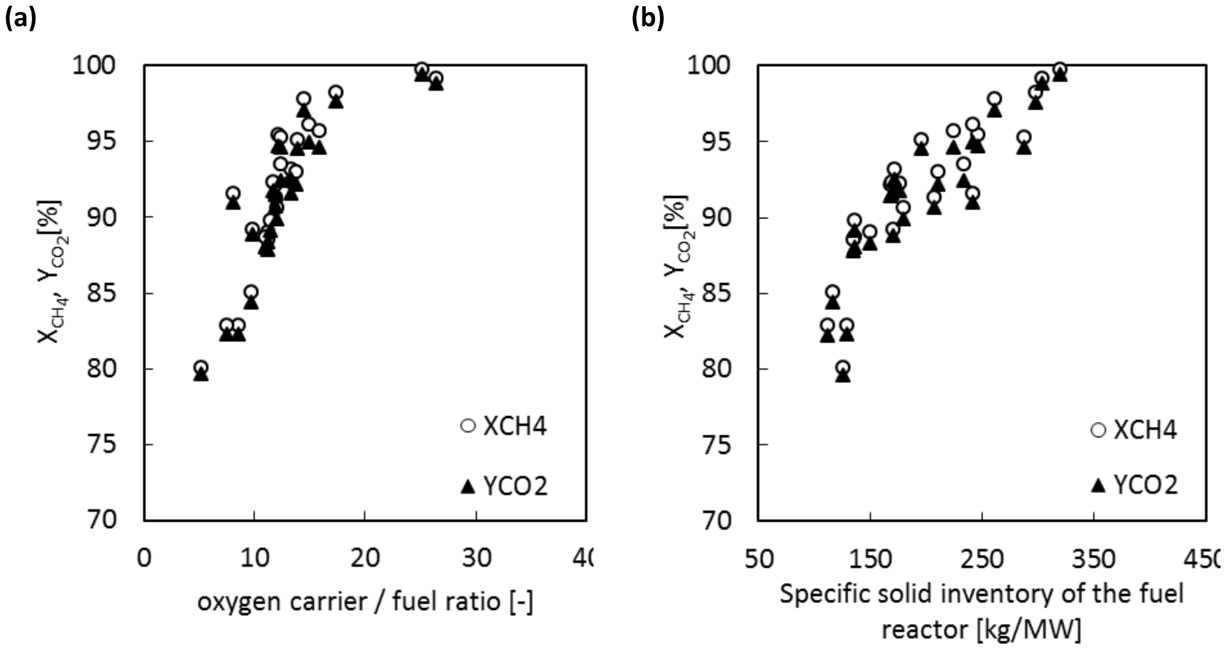

Figure 4.7: Main results of the C28 testing. (a) Influence of the oxygen carrier to fuel ratio on the fuel conversion, (b) Dependency of the fuel conversion on the specific inventory of the fuel reactor.

4.4 Development of a model describing the CLC process and measurement of reaction kinetics

Kinetics determination of C14 and C28

The kinetic of reactions involved in redox cycles of selected C14 and C28 oxygen carriers were determined; see Deliverable D4.2. Selected materials were $CaMnO_3$ based perovskite materials. C14 material includes Mg in the formula ($CaMn_{0.9}Mg_{0.1}O_{3-\delta}$), whereas C28 was further modified by titanium addition ($CaMg_{0.1}Ti_{0.125}Mn_{0.775}O_{3-\delta}$). Both materials showed oxygen uncoupling, but the oxygen transport capacity for CLOU was lower than the available oxygen transport capacity for reaction with a reducing gas.

Several redox cycles were performed to evaluate possible variations in reactivity and/or oxygen transport capacity of the materials. For C14, the reactivity was barely affected when the solid conversion variations during redox cycles were low; on the contrary, for higher variation of solids conversion the reactivity of C14 increased up to the 4th cycle, after which remains constant. The decrease in the oxygen transport capacity was due to the impossibility to oxidize the material up to the initial oxidation state after a reduction step. Particles that reached the maximum reactivity were denoted as "activated" material. The total oxygen transport capacity for fresh C14 particles was 10%, of which 1.1% corresponded to oxygen uncoupling. After activation, the total oxygen transport capacity decreased to 7.5%, and the oxygen uncoupling property was near lost.

The reactivity of C28 also increased with redox cycles. However, this material was more stable than C14 material regarding the oxygen transport capacity. The total oxygen transport capacity only decreased from 8.5% in fresh particles to 8.0% in activated particles. Moreover, the oxygen uncoupling property was maintained during redox cycles, with an oxygen loss of 1.4 wt.% at 1000°C in N_2.

The reactivity of C14 and C28 materials in a CLC system should depend on the variation of solids conversion reached in the fuel reactor. Therefore, kinetics for both fresh and "activated" particles were determined by thermogravimetric analysis. Conversion vs. time curves at different temperatures (973 - 1273K), and reacting gas concentration (5 - 60 vol.% for CH_4, H_2 or CO; 5 - 21 vol.% for O_2) were obtained for both fresh and activated materials. For kinetics determination, the shrinking core model with control by chemical reaction and diffusion through the product layer was used to obtain the kinetic parameters.

Development and validation of CLC model with C14

In this work, the upgrade of the mathematical model developed previously in the CLC Gas Power project is done both for the fuel and air reactors; see Deliverables 4.5 and 4.6. Both reactor models were developed in a general form to describe the fluid dynamic of a high-velocity fluidized-bed reactor, and later adapted to the fluid dynamics characteristics of the CLC unit, which is a Dual Circulating Fluidised Bed (DCFB) system. Kinetics for fresh C14 material was used instead of activated C14, as experimental evidence of non-activation was found when very high oxygen carrier circulation rate is used. Fresh C14 material has an important uncoupling activity. Thus, kinetics for oxygen uncoupling reaction was also included in the model.

The linking of the fuel reactor model with the air reactor model allows us to evaluate the global performance of the Dual Circulating Fluidised Bed (DCFB) system in the CLC process. Models are solved in an iterative way and the corresponding algorithms in FORTRAN code are developed. A time analogy is used to describe the convergence between both reactors.

The CLC model was validated against experimental results obtained in the CLC unit at Vienna University of Technology (TUV) using C14 material as oxygen carrier. For this purpose, theoretical predictions were compared to experimental results obtained under 29 different operational conditions, which detailed experimental results are available. The evaluation of the model accuracy was done by analysing the methane conversion and the oxygen carrier conversion in both reactors. In general, good fitting between theoretical and experimental results is obtained.

Methane conversion was affected by the operational conditions during the experimental campaign. The variation of methane conversion with operational conditions was evaluated by a detailed analysis of the theoretical results. In all conditions, the oxygen carrier was highly oxidized in the air reactor. So, oxygen carrier oxidation in the air reactor was not limiting the oxygen availability in the fuel reactor. Incomplete methane conversion was due to the low reactivity of C14 material with methane. However, near complete combustion was reached in some cases. Model results confirm this behaviour, and in these cases the relevance of oxygen transference via oxygen uncoupling mechanism became dominant over gas-solid reaction for methane conversion. An increase in the oxygen carrier to fuel ratio and the solids circulation flow rate values favour the oxygen transference by oxygen uncoupling mechanism, and hence the methane conversion is increased. The validated model is a powerful tool to simulate and optimize the CLC process.

WP5 Overall process integration and CLC next scale design

Overall process integration and CLC next scale design. Basic work was deliverable 5.1 where main parameters have been chosen. In deliverable 5.2 main data for CLC combustion were calculated and serve for final thermal calculation of the necessary heat exchangers and other equipment as well as operating data and cost estimation in deliverable 5.3. Deliverable 5.4 shows the hazards of different oxygen carrier materials and their surrogates. It was not possible to select one or two oxygen carrier materials, because till now it was not possible to find one material beside Ni which summarizes all necessary features for optimized use in CLC. The results in testing different materials are promising to find useable materials with good features and acceptable price. The remaining work in deliverable 5.5 was on the arrangement of the reactors for better connections of the oxygen carrier channels. The produced 3D pictures show additional a more realistic design with optimized layout of insulation and steel structure. Key facts of previous deliverables in workpackage 5:

Deliverable 5.1 Next scale CLC plant, report on deployment

In this description all parts of a 10 MW next CLC system and steam system are described only with main parameters and main dimensions.

- No special site conditions are needed – CLC can be adjusted
- Main design data for next scale: 10 MWth
- Steam parameters: 65bar, 450°C
- To show the possibility that CLC can operate an traditional steam cycle
- Based on the calculation results of Vienna University of Technology with process flow diagram and stream tab.

Deliverable 5.2 Integrated process model of a next scale CLC power plant
All basic data for further calculation of a next scale CLC power plant with 10 MW input have been calculated in 3 different conversion rates (ideal; average; real conversion). In accordance with EBTF (European Benchmark Task Force) some special boundary conditions have been choosen for a further basic calculation with average conversion.

- Process model work by Vienna University of Technology
- Optimization of the steam-cycle process

Deliverable 5.3 Economic assessment results and optimized process
The heat exchangers of the system are calculated with a special tool to design the important dimensions (Tubes; arrangement; pitch; channel width etc.). This calculation is used as basic design for layout and for calculation of costs.

- Optimized arrangement
- Calculation of costs
- Operating costs
- Specification of plant

Main components of the CLC/steam system:

CLC system

- Air reactor (AR)
- Cyclone after Air reactor
- Start-up burner
- Flue gas system after AR
- Fuel reactor (FR)
- Cyclone after Fuel reactor
- Flue gas system after FR
- Bed material cooler
- Flue gas Fan AR
- Flue gas Fan FR
- System for oxygen carrier

Steam System

- Steam drum
- Evaporator (walls of the Air reactor (AR))
- Heating surface (Super heater; Economiser; Air preheater) in flue gas stream after AR
- Evaporator heating surfaces in the bed material cooler
- Heating surface (Super heater and Economiser) in flue gas stream after FR
- Feed water tank with degasser
- Feed water pumps

- Fittings and pipelines
- Dosing system
- Sampling station

The boiler is designed with natural circulation system.

Design Criteria

The air reactor (AR) is designed on account of the exothermic reaction of the oxygen carrier with cooled walls. A lining with ceramic material serves for the protection of the walls. After AR cyclone the fortified oxygen carrier is separated from the exhaust gas from the AR. The exhaust gas is cooled in a flue gas system by means of superheater, economiser and airpreheater heating surfaces. The oxygen carrier is flowing after the AR cyclone partially to the bed material cooler (BMC) and partially to the Fuel reactor (FR). In the Fuel reactor the conversion of the fuel with the fortified oxygen carrier takes place. At the FR no cooling equipment is necessary and therefore the FR is not integrated in the natural circulation system. The exhaust gas from the FR is cooled in a separated flue gas system by means of superheater and Eco-heating surfaces. To control the temperature in the AR a certain heat quantity has to be transferred to the water/Steam system via the bed material cooler. Due to natural circulation the steam drum is on top of the plant, higher situated then the top of heating surfaces.

Construction

The boiler is designed in vertical, hanging design. The heating surfaces are inserted in lined channel cases.

Steam drum: The steam drum is designed according to usual directives in steam boiler construction.

Superheater: Every superheater bundle consists of horizontally and inline arranged plane tubes. The steam temperature is controlled to the demanded value about a certain load area by means of the surface cooler which is arranged in the steam drum.

Evaporator: The evaporator bundle (bed material cooler) is formed from inline arranged plane tubes and is inserted in a separate case.

Economiser: Every Economiser consists of horizontally and inline arranged plane tubes. All Economiser collectors are situated outside the flue gas stream.

Air preheater: The air preheater consists of horizontal and inline arranged plane tubes.

Bed material cooler (BMC): The BMC consists of horizontally and inline arranged plane tubes, as well as an entrance and an exit zone for the bed material. The bottom of BMC ground is provided with air nozzles to operate the oxygen carrier flow.

Costs of plant

For the calculation of costs a detailed micro calculation of all parts has been made. The prices for materials are prices based on middle European market in first quarter of 2013. It was assumed that CLC and common boiler have the same efficiency to provide a same calculation basis.

CLC Boiler plant:
Budget price for delivery and erection € 7.900.000.-
Common gas fired boiler:
Budget price for delivery and erection € 3.900.000.-

Deliverable 5.4 Environmental impact assessment for a specific application for one or two selected CLC oxygen carrier materials

- initial hazard evaluation
- ranking the potential occupational exposure hazards
- independent evaluation of human health and environmental hazards of substances used for chemical-looping combustion
- Table of oxygen carrier and surrogates for human health category assessment

- Green (small impact): MnO, MgO,Al2O3

Deliverable 5.5 Design review for next scale CLC plant

- Optimized design (arrangement of the reactors for smaller distances)
- More detailed and thus realistic design of the layout of the boiler, insulation and steel structure
- Comparison of operating costs with common fired boiler

Operating costs

It has to be considered that the different operation materials have a wide range in specific price. (natural gas; electric power;…) Only the following parameters have been considered for the operation costs.

- Natural gas
- Electric power
- Water
- O2 carrier

CLC Boiler plant

It is possible to say at this stage that the OC costs do not look prohibitive to development of CLC technology. Specially manganese - based OC seem to be lower in operation costs then nickel based OC.

Another very important figure for gaining money is the capture of CO2 with the CLC plant. But at the moment an indication of a certain benefit is not possible. The captured quantity of CO2 is 2000 kg/h.

Comparing operation costs between common boiler and CLC boiler with the before given values results in following diagram.

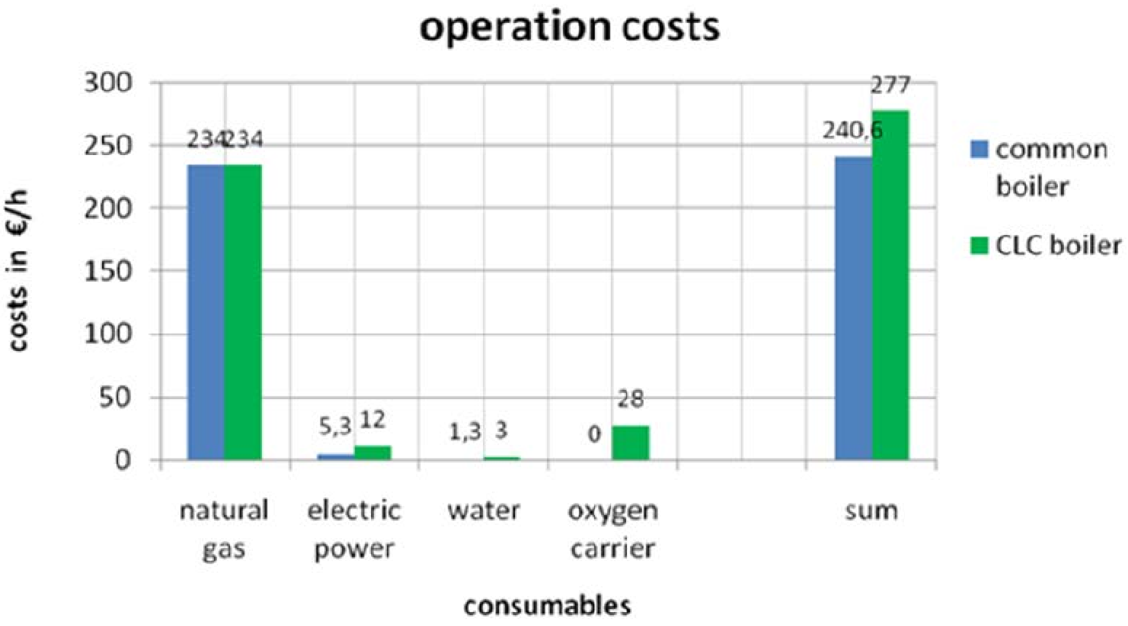

Figure 5.1 Cost comparison between CLC boiler and ordinary natural gas boiler.

Lay out

To give an overview for a next scale plant a 3D layout was designed with the components described before. System with steel structure and insulation

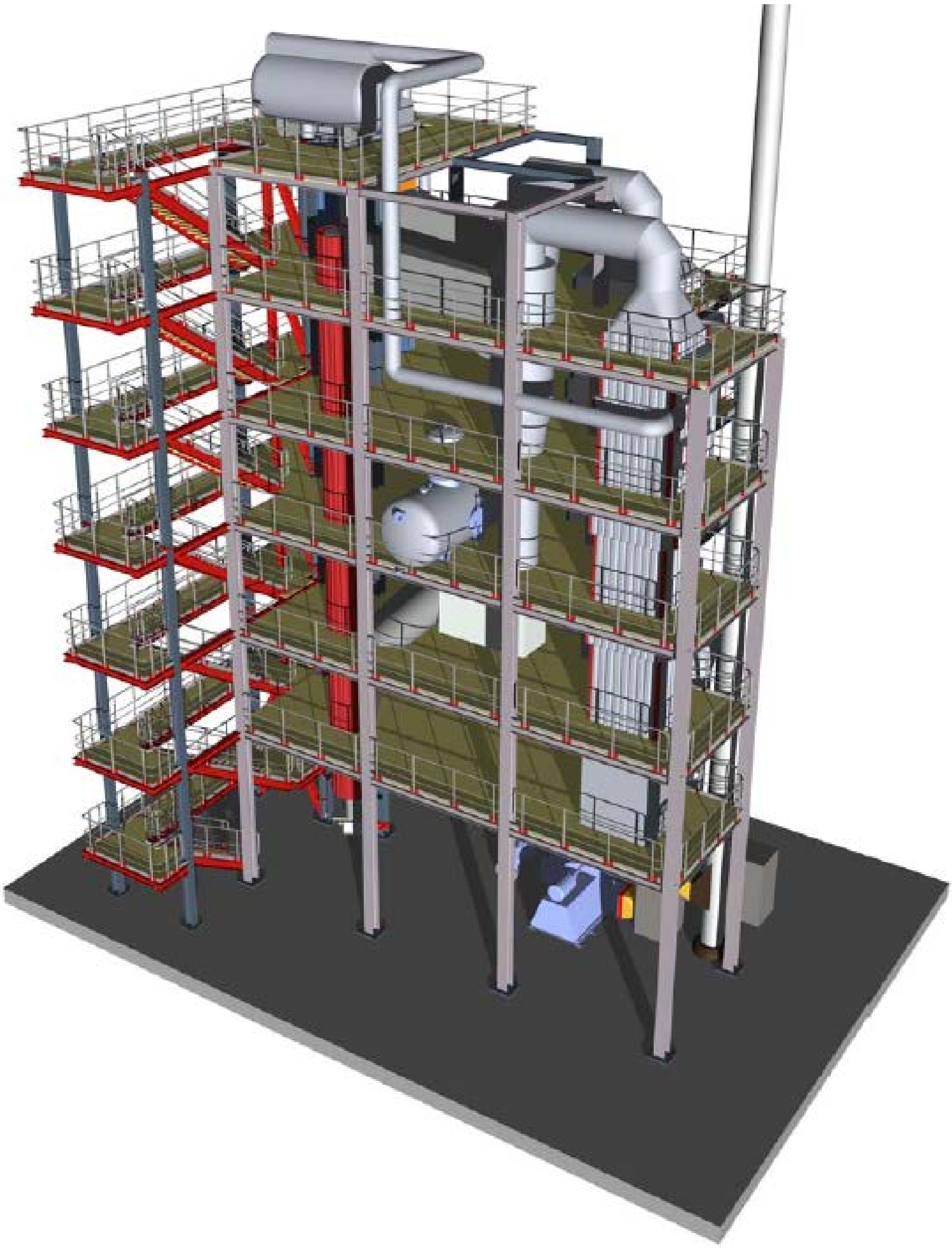

Figure 5.2 Rendering of proposed CLC plant.

Conclusion

Layout: For the present layout all heating surfaces without air preheater are designed with plane tubes. With operation experience on a next scale plant, it would be possible to design the superheater and economiser heating surfaces with finned tubes. This would mainly result in lower investment costs and other arrangement of channels.

Costs for the plant: Due to the need of two reactors, the divided flue gas streams and the oxygen carrier system the CLC Boiler is much more expensive than a common gas fired boiler. In future, when more operation experience with CLC systems is gathered, some price relevant optimization can be made to lower the price of CLC boilers, but always a big difference to common boiler will remain for the wanted CO2 separation.

Personnel costs: A comparison between CLC boiler and common boilers only seems to be relevant, when CLC boilers have been operated for several 1000 hours. Due to the higher amount of mechanical parts (especially the oxygen carrier flow parts) higher personnel expenditure will remain even when the normal operation can be driven automatically.

Operation costs: Costs for natural gas are naturally the same (CLC compared to common boiler). Costs for water are higher at CLC, but the figure is not very relevant. Costs for electric power consumption for CLC boiler are considerable higher. Costs for oxygen carrier are the most relevant operation costs beside natural gas at the momentarily stage of development.

Financial costs: With the given values in this deliverable, a basic financial statement can be made if wanted and the financial aspects are clearly defined.

Oxygen Carrier: In the actual calculation of operating costs when consumables are regarded only, the costs for oxygen carrier need appr. 15% of the total operating cost. In reality, when personnel and financial costs are being also considered, this share will get significant lower and oxygen carrier costs are not crucial for a CLC project. Most important issues are attrition rate, the O2 capacity and the hazards of new oxygen carrier material.

CO2 Capture: The flue gas from the AR behind the last economiser bundle resp. behind the SR ID fan contains appr. 1/3 of CO2 and 2/3 of H2O. The next step in CO2 processing is to condensate the share of water. Further steps are compressing and liquifying if necessary. A very important question is the question on benefit for environment for each captured ton of CO2.

Use and dissemination of foreground

Dissemination of the public information was organized mainly by publications in scientific journals and by participation to international conferences organized on CO2 capture technologies and fluidized bed technologies:

- At start-up of the project the ambition was to submit at least 12 publications to peer-reviewed scientific journals, and at least 10 abstracts to relevant international conferences. This ambition has been fulfilled. At present, 5 scientific articles have been accepted for and published in peer reviewed papers, 5 more have been submitted and are currently under review, and another 5 articles will be submitted in the near future. This means that the output from the project with respect to peer reviewed articles should be in the range 15 papers.
- As for representation at international conferences more than 25 individual presentations have been held. Out of these 12 are associated with the two public workshops being arranged as a part of the project, while the remaining 13 were at various international conferences and workshops. Presentations have been held at several of the most important conference series within the field such as the International Conference on Greenhouse Gas Control Technologies, International Conference on Chemical Looping, International Conference on Fluidized Bed Combustion, High Temperature Solid Looping Network Meeting and the Trondheim CCS Conference.

Further, research results in a range from general public information to high quality scientific publications was also published or made available in open reports. For this purpose a home page available on internet (www.clc-innocuous.eu) was created and maintained during the project. Generally, only unrestricted reports were made directly accessible to the public. This does not mean that results reported in deliverables classified as CO or RE will not be made public. It means that the results will first be carefully examined to ascertain that intellectual property rights are protected before publication, and, moreover, that presentation of results will be further processed, e.g. to meet the standards of high quality scientific journals or the format suitable for communicating results to a wider audience. Effective and efficient approval procedures agreed in the consortium agreement helped minimize time delays for publications and dissemination. Moreover the beneficiaries also organize two public work-shops to which companies and organisations with potential interest in this technology were invited.

Section A (public)

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES										
NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers (if available)	Is/Will open access provided to this publication?
1	*$CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ as Oxygen Carrier in a Gas-Fired 10 kWth Chemical-Looping Combustion Unit*	*Källén, M*	*Industrial and Engineering Chemistry Research*	*Vol 52, No 21*	*ACS*		*2013*	*pp. 6923-6932*	http://publications.lib.chalmers.se /records/fulltext/177314/local_177314.pdf	yes
2	*Performance of a low Ni content oxygen carrier for fuel gas combustion in a continuous CLC unit using a CaO/Al_2O_3 system as support.*	*Gayán, P*	*International Journal of Greenhouse Gas Control*	*Vol 14*	*Elsevier*		*2013*	*pp. 209-219*	http://digital.csic.es/handle/10261/79116	yes
3	*Chemical Looping with Oxygen Uncoupling experiments in a batch reactor using spray dried $CaMn_{(1-x)}M_xO_{3-\delta}$ (M=Ti, Fe, Mg) particles as Oxygen Carriers*	*Hallberg, P*	*Energy and Fuels*	*Vol 27, No 3*	*ACS*		*2013*	*pp. 1473-1481*	http://publications.lib.chalmers.se /publication/180068	yes
4	*Use of chemically and physically mixed iron and nickel oxides as oxygen carriers for gas combustion in a CLC process*	*Pans, M A*	*Fuel Processing Technology*	*Vol 115*	*Elsevier*		*2013*	*pp. 152-163*	http://digital.csic.es/handle/10261/79120	yes

5	*Examination of perovskite structure CaMnO3-d with MgO addition as oxygen carrier for chemical looping with oxygen uncoupling using methane and syngas*	*Jing, D*	*International Journal of Chemical Engineering*	*Article ID 679560, DOI:10.1155/2013/679560*	*Hindawi*		*2013*		http://www.hindawi.com/journals/ijce/2013/679560/	yes
6	*Fate of sulphur during CLC using an impregnated Fe-based oxygen carrier*	*Cabello, A*	*Submitted for publication*							yes
7	*Measuring attrition resistance of oxygen-carrier particles for chemical-looping combustion with a customized jet cup*	*Rydén, M*	*Submitted for publication*							yes
8	*Relevance of the catalytic activity on the performance of a NiO/CaAl2O4 oxygen carrier in a CLC process*	*Cabello, A*	*Submitted for publication*							yes
9	*Reduction and Oxidation Kinetics of CaMn0.9Mg 0.1O 3-δ Oxygen Carrier for Chemical Looping Combustion*	*de Diego, F*	*Submitted for publication*							yes
10	*Effect of operating conditions and H2S presence on CaMn0.9Mg 0.1O 3-δ perovskite material performance in CLC*	*Cabello, A*	*Submitted for publication*							yes
11	*CuO-based oxygen-carrier particles for chemical-looping with oxygen*	*Rydén, M*	*To be submitted*							yes

	uncoupling (CLOU) – experiments in batch reactor and in continuous operation.									
12	*CaMnO3-δ based oxygen carriers used in continuous Chemical-Looping Combustion*	*Hallberg, P*	*To be submitted*							yes
13	*Combined Oxides of Iron, Manganese and Silica as Oxygen Carriers for Chemical-Looping with Oxygen Uncoupling*	*Källén, M*	*To be submitted*							yes
14	*(title not set)*	*Mayer, K.*	*Manuscript in preparation*							yes
15	*(title not set)*	*Hallberg ,Källén*	*Manuscript in preparation*							yes

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

NO.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed
1	*Conference oral presentation: Innocuous - Innovative Oxygen Carriers Uplifting Chemical-Looping Combustion (CLC)*	*Lyngfelt, A*	*Carbon Capture, Transport and Storage: R&D to Implementation*	*24-26 May 2011*	*London, U.K.*	*Scientific Community, Industry*		
2	*Conference oral presentation: Introduction to INNOCUOUS*	*Lyngfelt, A*	*Innocuous 1st public workshop*	*August 31, 2011*	*Vienna, Austria*	*Scientific Community, Industry*	*100*	
3	*Conference oral presentation: New combined oxide materials*	*Hallberg, P*	*Innocuous 1st public workshop*	*August 31, 2011*	*Vienna, Austria*	*Scientific Community, Industry*	*100*	
4	*Conference oral presentation: Chemical-looping combustion of gaseous fuels with synthetic Fe and Cu based oxygen carriers*	*Adánez, J*	*Innocuous 1st public workshop*	*August 31, 2011*	*Vienna, Austria*	*Scientific Community, Industry*	*100*	
5	*Conference oral presentation: Scaleup of O-carrier production for Chemical Looping Combustion by spray drying*	*Van Noyen, J*	*Innocuous 1st public workshop*	*August 31, 2011*	*Vienna, Austria*	*Scientific Community, Industry*	*100*	
6	*Conference oral presentation: Effect of sulfur and higher hydrocarbons on*	*Mayer, K*	*Innocuous 1st public workshop*	*August 31, 2011*	*Vienna, Austria*	*Scientific Community, Industry*	*100*	

	chemical looping combustion in a 120 kW pilot plant							
7	*Conference oral presentation: Overall process integration and CLC next scale design*	*Bertsch, O*	*Innocuous 1st public workshop*	*August 31, 2011*	*Vienna, Austria*	*Scientific Community, Industry*	*100*	
8	*Conference presentation*: Next Scale Chemical Looping Combustion: Fluidized Bed System Desgin for Demonstration Unit*	*Marx, K*	*21st International Conference on Fluidized Bed Combustion*	*June 3-6, 2012*	*Naples, Italy*	*Scientific Community*		
9	*Conference oral presentation: Particle Characteristics for CLC and Overview of INNOCUOUS Project*	*Williams, G*	*IChemE Particle Technology Special Interest Group*	*June 25, 2012.*	*London, U.K.*	*Scientific Community, Industry*		
10	*Conference oral presentation**: Developing a Highly Reactive and Low Nickel Content Oxygen Carrier for Gaseous Fuels in CLC*	*Gayán, P*	*2nd International Conference on Chemical Looping*	*26-28 September 2012*	*Darmstadt, Germany*	*Scientific Community*	*150*	
11	*Conference presentation***: Manganese silica combined oxide as oxygen carrier for chemical-looping combustion*	*Jing, D*	*2nd International Conference on Chemical Looping*	*26-28 September 2012*	*Darmstadt, Germany*	*Scientific Community*	*150*	
12	*Conference oral presentation: Spray Drying – a scale up ready preparation technique for oxygen carrier production*	*Van Noyen, J*	*2nd International Conference on Chemical Looping*	*26-28 September 2012*	*Darmstadt, Germany*	*Scientific Community*	*150*	
13	*Conference oral presentation: Chemical*	*Karimi, S*	*TÜV SÜD NEL Ltd - CCS*	*November 14, 2012*	*Edinburgh, U.K.*	*Scientific Community,*		

	Looping Combustion & INNOCUOUS		*Technology Club Meeting*			*Industry*		
14	*Conference presentation****: Next scale chemical looping combustion: Process integration and part load investigation for a 10MW demonstration unit*	*Marx, K*	*11th International Conference on GHGT*	*18-22 November 2012*	*Kyoto, Japan*	*Scientific Community*		
15	*Conference oral presentation*****: Evaluation of a highly reactive and sulfur resistant synthetic Fe-based oxygen carrier for CLC using gaseous fuels*	*Gayán, P*	*11th International Conference on GHGT*	*18-22 November 2012*	*Kyoto, Japan*	*Scientific Community*		
16	*Conference poster presentation******: Innovative Oxygen Carrier Materials for Chemical Looping Combustion*	*Jing, D*	*11th International Conference on GHGT*	*18-22 November 2012*	*Kyoto, Japan*	*Scientific Community*		
17	*Conference oral presentation: O-carrier production for Chemical Looping Combustion by Spray Drying*	*Van Noyen, J*	*Innocuous 2nd public workshop*	*28 May, 2013*	*Antwerp, Belgium*	*Scientific Community, industry*	*90*	
18	*Conference oral presentation: Results with combined oxides in laboratory and in long-term operation*	*Mattisson, T*	*Innocuous 2nd public workshop*	*28 May, 2013*	*Antwerp, Belgium*	*Scientific Community, industry*	*90*	
19	*Conference oral presentation: Long term operation of new oxygen carriers with no Ni content during gas combustion in*	*Adánez, J*	*Innocuous 2nd public workshop*	*28 May, 2013*	*Antwerp, Belgium*	*Scientific Community, industry*	*90*	

	CLC							
20	*Conference oral presentation: HSE aspects of CCS technologies*	*Smulders, C*	*Innocuous 2nd public workshop*	*28May, 2013*	*Antwerp, Belgium*	*Scientific Community, industry*	*90*	
21	*Conference oral presentation: Chemical looping combustion under relevant conditions using different oxygen carriers in a 120 kW pilot plant*	*Mayer, K*	*Innocuous 2nd public workshop*	*29 May, 2013*	*Antwerp, Belgium*	*Scientific Community, industry*	*90*	
22	*Conference oral presentation: CLC overall process integration*	*Hofmann, R*	*Innocuous 2nd public workshop*	*29 May, 2013*	*Antwerp, Belgium*	*Scientific Community, industry*	*90*	
23	*Conference oral presentation******: (Fe1-xMnx)TiyO3 based oxygen carriers for chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU)*	*Rydén, M*	*7th Trondheim CCS Conference*	*June 5, 2013*	*Trondheim, Norway*	*Scientific Community*	*70*	
24	*Conference oral presentation: Spray drying as scale-up ready technique for manufacture of oxygen carrier particles for chemical looping*	*Van Noyen, J*	*6th International Granulation Workshop*	*27 June, 2013*	*Sheffield, U.K.*	*Scientific Community*		
25	*Pilot plant testing of Fe- and Mn-based oxygen carriers for chemical looping combustion*	*Mayer, K*	*5th High Temperature Solid Looping Network Meeting*	*2-3 September 2013*	*Cambridge, U.K.*	*Scientific Community*		

The following presentations are associated with conference publications:

** Marx, K., Pröll, T., Hofbauer, H., 2012, "Next Scale Chemical Looping Combustion: Fluidized Bed System Design for Demonstration Unit", in:*

Proceedings of the 21st International Conference on Fluidized Bed Combustion (FBC), 3.-6. June 2012, Naples, Italy, pp.269-279, ISBN978-88-89677-83-4.

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