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**Project acronym:**
SUCCESS

**Project full title:**
Industrial steam generation with 100% carbon capture and insignificant efficiency penalty - scale-up of oxygen carrier for chemical-looping combustion using Environmentally sustainable materials

**Collaborative project**

**Theme:**
FP7 – ENERGY.2013.5.1.1

# Deliverable D9.6

# Summary of public workshop II

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**Dissemination level**:
Restricted (RE)

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# Summary of public workshop II

| | |
|---|---|
| **SUCCESS** - Industrial steam generation with 100% carbon capture and insignificant efficiency penalty - scale-up of oxygen carrier for chemical-looping combustion using Environmentally sustainable materials | **Keywords**: Dissemination, public work shop |
| **Work package**: 9 – Dissemination | |
| **Related Task:** Task 9.1 | |
| **Involved partners**: Vienna | **Dissemination level**: Restricted (RE) |

**Objective**

The deliverable summarizes the contributions to the planned 2nd public workshop which will be held during the Trondheim Conference on $CO_2$ Capture, Transport and Storage (TCCS-9) from June 12-14, 2017 in Trondheim.

# Table of Contents

# 1 Introduction

The SUCCESS project will host two public workshops where (preliminary) results will be communicated. Additionally, a project flyer including a project description, objectives and preliminary results will be distributed at the workshops. It was decided during the regular face-to-face meeting in December 2016 hosted by partner Chalmers to have the second public workshop together with the *9th "Trondheim Conference on $CO_2$ Capture, Transport and Storage"* (TCCS-9), which will be held June 12-14, 2017, in Trondheim, Norway. The conference is organized by NCCS – International CCS Research Centre under auspices of NTNU Trondheim and SINTEF.

The idea behind holding the workshop within this conference was to address stakeholders within the whole value chain of Carbon Capture and Storage technology development. It was regarded as important by the consortium that the later results of the project, i.e. scale-up to 1 MW fuel power and results from pilot operation, will be presented at the second workshop to show the whole picture of the project and its results. Since these results were not ready before the very end of the project, it was decided to have the second workshop after the end of the project as side event of TCCS-9.

# 2 Hosting event

The TCCS is a series of conferences hosted by SINTEF and NTNU Trondheim. Topics and contributions cover the whole CCS value chain from capture to storage. The target group of the conference are participants from R&D institutions, universities and industry. The conference covers the following topics:

1. Pre-combustion capture
2. Post-combustion capture
3. Oxy-fuel capture
4. CCS and hydrogen combinations
5. CCUS
6. Storage
7. $CO_2$ and EOR
8. International and R&D activities including pilot and large scale activities
9. Novel technologies
10. Public acceptance and communication
11. CCS whole system issues

# 3 Contributions by SUCCESS

The Focus of the second public workshop was on results from material testing in the smaller pilot units up to 150 kW, scale-up of the technology to 1 MW in Darmstadt as well as results from end-user evaluation. This will include environmental impact studies, life cycle analysis and techno-economic evaluation. In detail, the following ten presentations will be held at the second public workshop:

| Authors | Partners | Title |
|---|---|---|
| Marijke Jacobs, Tjalling van der Kolk, Knuth Albertsen, Tobias Mattisson, Anders Lyngfelt, Frans Snijkers | VITO, ESAM, Chalmers | Synthesis and upscaling of perovskite Mn-based oxygen carrier by industrial spray drying route |
| A. Cabello, P. Gayán, J. Adánez, F. García-Labiano, L. F. de Diego, M.T. Izquierdo, A. Abad, A. Scullard, G. Williams | CSIC, JM | Developing industrially scalable Cu-based oxygen carriers for Chemical Looping Combustion by impregnation and granulation routes |
| Tobias Mattisson, Patrick Moldenhauer, Peter Hallberg, Frans Snijkers, Marijke Jacobs, Knuth Albertsen, Gareth Williams, Andrew Scullard, Anders Lyngfelt | Chalmers, VITO, ESAM, JM | Testing of innovative Fe- and Ca-Mn-based oxygen carriers with natural gas in continuous operation |
| A. Tilland, A. Lambert, W. Pelletant, D. Chiche, C. Bounie, S. Bertholin | IFP | Comparison of two oxygen carriers performances for Chemical Looping Combustion application |
| Karl Mayer, Robert Pachler, Stefan Penthor, Hermann Hofbauer | Vienna | Testing of two commercially produced oxygen carrier materials in a 120 kW CLC pilot unit |
| Øyvind Langørgen, Inge Saanum, Nils Erland L. Haugen | SINTEF ER | Chemical looping combustion of methane using copper oxide and calcium-manganite oxygen carriers in a 150 $kW_{th}$ reactor system for gaseous fuels |
| Peter Ohlemüller, Michael Reitz, Jochen Ströhle, Bernd Epple | TUD | Operation of a 1 $MW_{th}$ chemical looping pilot plant with natural gas |
| Ziad Hamidouche, Enrica Masi, Pascal Fede, Hervé Neau, Olivier Simonin, Karl Mayer, Stefan Penthor and Juan Adanez | INPT, Vienna, CSIC | Coupling between gas-solid reaction modeling and CFD multiphase approach for 3D numerical simulation of a 120 kWth CLC unit and comparison with experimental data |
| L. Geerts, R. Weltens, H. Witters, Y. Davila, A. El Aissami, E. Frijns, J. Bergmans, K. Boonen, F. Snijkers | VITO, Shell | Scale-Up of oxygen Carrier for Chemical-looping combustion using Environmentally SuStainable materials (SUCCESS) – Health & safety assessment, Life Cycle Analysis and recycling options |
| Florian Zerobin, Tobias Pröll, Stefan Penthor, Otmar Bertsch and Olivier Authier | BOKU, Vienna, Bertsch, EDF | Chemical looping combustion for power and steam generation from natural gas – process arrangements and expectable performance |

# 4 Abstracts of SUCCESS contributions

The public workshop was part of Track 3 (Carbon Capture and Utilization) with a dedicated session for SUCCESS. Thus, participation was open for all participants of the BSDS conference and it is not possible to quantify and name participants of the workshop. However, the following pages present a list of participants of the conference, including names and affiliations.

## 4.1 Introduction to Mn based oxygen carrier material

**Synthesis and upscaling of perovskite Mn-based oxygen carrier by industrial spray drying route**

Marijke Jacobs[a], Tjalling van der Kolk[b], Knuth Albertsen[b], Tobias Mattisson[c], Anders Lyngfelt[c], Frans Snijkers[a]

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[b]*EuroSupport Advanced Materials, Liessentstraat 9f, 5405 AH Uden, The Netherlands*
[c]*Department of Energy and Environment, Energy Technology Division, Chalmers University of Technology, S-412 96 Gothenburg, Sweden*

**Abstract**

Chemical looping combustion (CLC) has inherent separation of the greenhouse gas $CO_2$ and is often configured as two coupled fluidized bed boilers (CFB) thus avoiding direct contact between air and fuel. The transfer of oxygen is realised by metal oxide particles that continuously circulate between the two reactors. By removal of the water relatively pure $CO_2$ is obtained in a separate exhaust stream from the fuel reactor, making energy consuming flue gas separation unnecessary. Mn-based oxygen carrier materials have so called CLOU properties: they release oxygen to the gas phase. However, pure Mn-oxides suffer from unfavourable kinetics and thermodynamics to be applicable as oxygen carrier. To solve this problem, Mn can be combined with other metal oxides cations resulting in oxygen carrier material with perovkite crystal structure that have superior performance.

Combined Mn-based oxygen carriers materials can be prepared by the industrial spray drying technique. Spray drying is an industrial, one-step, continuous particle-processing operation that transforms a fluid state into a dried particulate form. As a result, spray dried oxygen carrier particles can be obtained with a high sphericity, good free-flowing and fluidization properties and homogeneity on the micron-scale. In order for these oxygen carriers to be viable for use in a power plant it is important that the raw materials can be obtained in large quantities at a reasonable cost. This paper focuses on the upscaled fabrication of highly promising perovskite $CaMn_{0,775}Ti_{0,1}Mg_{0,1}O_3$ oxygen carriers with the industrial spray drying technique. In the EC FP7 project SUCCESS innovative oxygen carriers of this composition have been prepared using abundant and cheap raw materials. It is shown that manganese ores and refined oxides can be used. A major part of the research effort is being devoted to scale-up the oxygen carrier fabrication route. The importance of specific process parameters for the functional behaviour of oxygen carrier particles like fluidization, reactivity and attrition properties will be addressed.

## 4.2 Introduction to Cu based oxygen carrier material

**Developing industrially scalable Cu-based oxygen carriers for Chemical Looping Combustion by impregnation and granulation routes**

A. Cabello[a], P. Gayán[a], J. Adánez[a], F. García-Labiano[a], L. F. de Diego[a], M.T. Izquierdo[a], A. Abad[a], A. Scullard[b], G. Williams[b]

[a]*Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, 50018-Zaragoza, Spain*
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**Abstract**

Chemical Looping Combustion, CLC, is one of the most promising processes to capture $CO_2$ at a low cost. It is based on the transfer of the oxygen from air to the fuel by using a solid oxygen carrier that circulates between two interconnected fluidized-bed reactors: the fuel- and the airreactor. The $CO_2$ capture is inherent to this process, as the air does not get mixed with the fuel. The key issue in the system performance is the oxygen carrier material. The oxygen carrier must fulfil several characteristics such as high reactivity and good fluidization properties that will rely on their redox system and the support. Moreover, the method used in the preparation of the materials strongly affects the properties of the oxygen carrier. Another important feature of an oxygen carrier is its particle lifetime that has an important impact on process cost. The particle lifetime of an oxygen carrier is related to its attrition behaviour, an important characteristic for its use in fluidized bed reactors. The CLC process is still under development waiting for a large scale demonstration experience. Therefore, the identification of raw materials, available at multi-ton scale at a competitive price, is one of requirements for the success of the technology. Promising impregnated oxygen carriers have been developed to perform well for gaseous fuels, although they were prepared from supports that are not available for commercial scale production. Inside the EU FP7-SUCCESS project, the identification of raw materials, available at multi-ton scale at a competitive price and suitable for well-performing impregnated oxygen carriers, has been one of the targeted objectives.

The purpose of this work is to evaluate the performance of different scalable materials based on Cu for methane combustion and then to identify the best material based on reactivity and attrition resistance. On the one hand, an industrial partner, Johnson Matthey, prepared different impregnated Cu-based materials using supports from different suppliers and raw materials ($ZrO_2$, $SiO_2$, and $Al_2O_3$). On the other hand, granulated materials based on copper and low-priced alumina were also prepared to reduce the cost of oxygen carrier industrial scale production and to evaluate the effect of the preparation route on the particle behaviour.

Several techniques were used to physically and chemically characterize the different materials prepared (crushing strength, ASTM attrition index, X-ray diffraction analysis, SEM-EDX analysis, total active metal content, oxygen transport capacity, and methane and hydrogen reactivity by TGA). Moreover, selected materials were evaluated in methane combustion tests in a continuous 500 $W_{th}$ CLC unit. More than 175 h of combustion operation were carried out to analyse combustion efficiency, active metal content and attrition rate.

A granulated Cu-based material can be selected based on its suitable attrition index and reactivity. However, an impregnated oxygen carrier prepared using a commercial alumina as support, with outstanding results in terms of both combustion efficiency and mechanical stability, was proposed as the best oxygen carrier for scaled-up CLC technology for gaseous fuels. Complete fuel combustion was achieved at low oxygen carrier to fuel ratio values (1.5–2.0) with a particle lifetime of 5000 h.

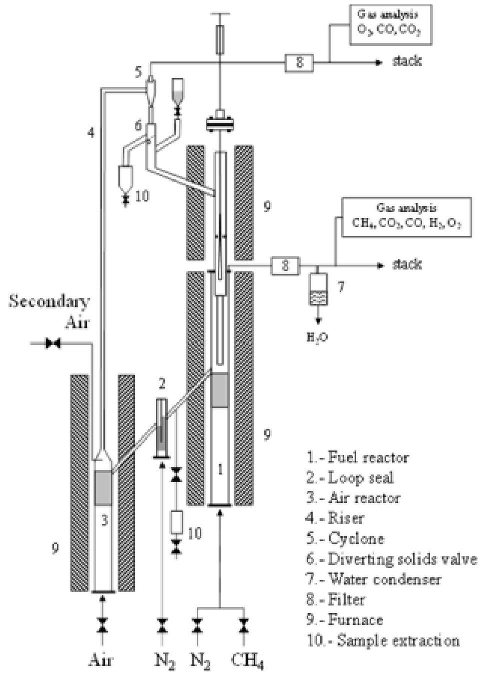


*Figure 1: Schematic diagram of the continuous 500 Wth CLC prototype.*

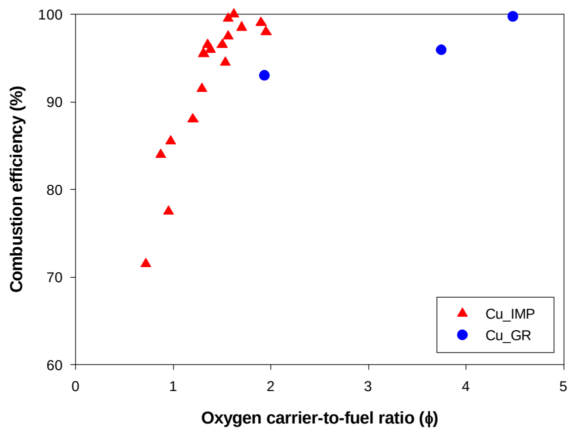


*Figure 2: Effect of the oxygen carrier-to-fuel ratio on the combustion on the combustion efficiency with the impregnated ($T_{FR}$=800°C, $T_{AR}$=800°C) and granulated ($T_{FR}$=900°C, $T_{AR}$=900°C) oxygen carriers tested in the continuous 500 $W_{th}$ CLC unit.*

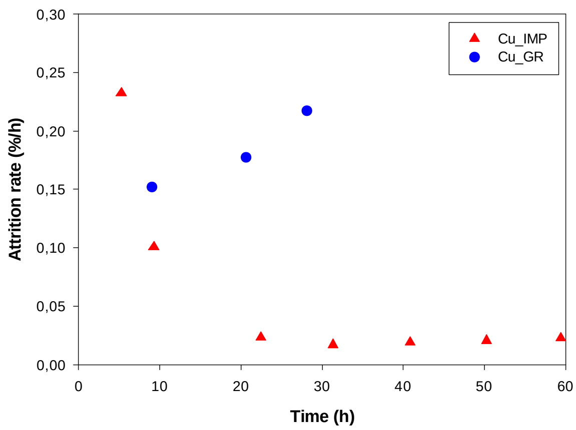


*Figure 3: Attrition rate profile of the impregnated and granulated Cu based oxygen carrier tested in the continuous 500 $W_{th}$ CLC unit.*

## 4.3 Oxygen carrier material testing at 10 kW (Chalmers)

### Testing of innovative Fe- and Ca-Mn-based oxygen carriers with natural gas in continuous operation

Tobias Mattisson[a], Patrick Moldenhauer[a], Peter Hallberg[a], Frans Snijkers[b], Marijke Jacobs[b], Knuth Albertsen[c], Gareth Williams[d], Andrew Scullard[d], Anders Lyngfelt[a]

*[a]Department of Energy and Environment, Division of Energy Technology, Chalmers University of Technology, S-412 96 Gothenburg, Sweden, [b]Flemish Institute for Technological Research (VITO), Unit Sustainable Materials Management, Boeretang 200, B-2400 Mol, Belgium, [c]Eurosupport Advanced Materials, Liessentstraat 9f, 5404 AH Uden, The Netherlands, [d]Johnson Matthey, Blount's Court, Sonning Common, Reading RG4 9NH, United*

**Abstract**

Chemical-looping combustion (CLC) of gaseous fuels, such as natural or refinery gas, could be a viable option in a variety of industries for production of heat and electricity with CCS. Further, CLC can be combined with conventional steam–methane reforming for efficient carbon-neutral hydrogen production. A series of collaborate European projects have been carried out since 2002, which focused on oxygen-carrier development and upscaling of both the CLC process and oxygen-carrier production with natural gas and refinery gas as fuel. In the latest project, SUCCESS (2013-2017), a series of oxygen carriers based on Fe and Ca-Mn materials were developed using commercial and low-cost raw materials. Two commercial methods for particle production were used: impregnation of $Fe_2O_3$ on $Al_2O_3$ and spray-drying of $CaMnO_3$. In this paper, selected results are presented from investigation of these two promising oxygen carriers using a laboratory-scale unit with continuous operation and a nominal fuel input of 10 $kW_{th}$. In this unit, the gas velocities in the riser and in the grid jet zone of the gas distributor come close to gas velocities of industrial-scale units and the material is exposed to a large number of redox cycles. Therefore, this unit is highly applicable for judging particle lifetime. Both materials functioned well during operation with natural gas, with little or no agglomeration. The total time with fuel was 30 h and >100 h for the impregnated Fe-based material and the Ca-Mn-based material, respectively. Although the degree of elutriation was high for both materials, the actual fines production (<45 μm) was high only initially, but decreased as a function of time. Almost full gas yield to $CO_2$ could be obtained with the spray-dried Ca-Mn-based material, and up to 85% yield was obtained with the impregnated oxygen carrier based on Fe at 950°C.

## 4.4 Oxygen carrier testing at 10 kW (IFPEN)

### Comparison of two oxygen carriers performances for Chemical Looping Combustion application

A. Tilland, A. Lambert, W. Pelletant, D. Chiche, C. Bounie, S. Bertholin

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**Abstract**

The chemical looping combustion (CLC) process is a promising technology of energy production with inherent $CO_2$ capture. Over the years, various international projects have participated to the development of the CLC process, and more specifically to the improvement of oxygen carrier materials in terms of reactivity and lifetime. This is the case for the present study which has been conducted in the framework of the FP7 SUCCESS project, the aim of which is the scale-up of oxygen carrier production using environmentally sustainable raw materials. The objective here was to compare the CLC process performance of two oxygen carriers selected and produced within the project: a copper based material (impregnated $CuO/Al_2O_3$) and a perovskite material (spray-dried $CaMn_{0.775}Mg_{0.1}Ti_{0.125}O_{3-\delta}$).

The evaluation of both materials has been carried out using two different pilot units :

- a fixed bed reactor which has been used for kinetic determination at different temperatures. A model of this reactor has been developed in order to determine the kinetic parameters of the kinetic laws selected for both materials. This model has then been used to properly compare the materials under similar operating conditions and calculate the reaction rates values along the reactor abscissa (figure 1 (a)),
- A continuous pilot plant at 10 $kW_{th}$ scale which has been used to characterize the ageing of the material over time. The performances of the unit have been calculated at constant operating conditions during more than 40 h and 270h of continuous operation for perovskite and copper based material respectively (results of the copper based material presented in figure 1 (b)). Several characterization methods have been used to describe the material's degradation over time.

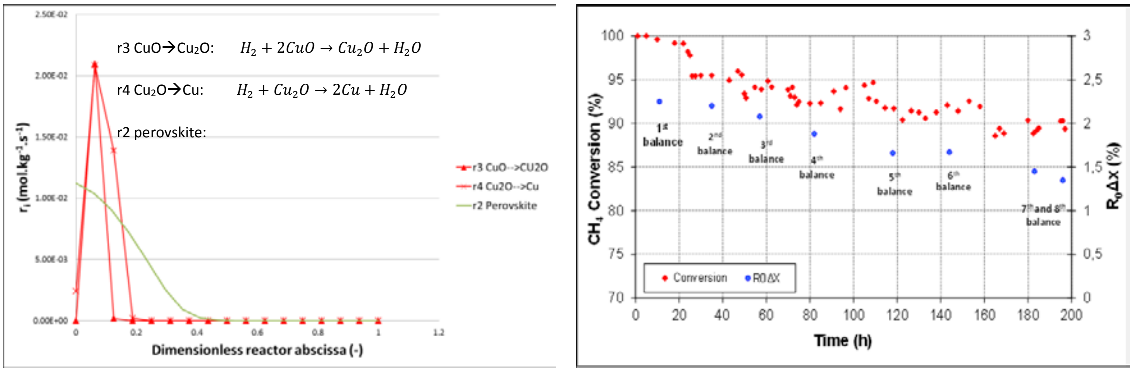


*Figure 1: (a) Reaction rate of $H_2$ oxidation for both material along the fixed bed reactor and (b) Reactivity decrease of the copper based material over time in the pilot plant*

The analysis of these results allows to bring out the advantages and drawbacks of both materials and to compare of their performances. According to our results and operating conditions, the copper based material seems more attractive in term of reactivity but should be operated at a low degree of reduction to avoid CO and $H_2$ formation. On the other hand, the perovskite material presents better attrition resistance in the initial state even if degradation over time is observed for both materials.

## 4.5 Oxygen carrier material testing at 120 kW

### Testing of two commercially produced oxygen carrier materials in a 120 kW CLC pilot unit

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**Abstract**

Inherent $CO_2$ separation in a combustion process can be achieved with Chemical looping combustion (CLC). Oxygen is transported with an oxygen carrier material from a so called air-reactor to the fuel-reactor. Mixing of combustion air and fuel is avoided and two off gas streams are generated. One consisting of oxygen depleted air and the other of one contains only $CO_2$ and steam.

CLC with gaseous fuels is by now ready for upscaling to commercial scale. A big issue in this process is the manufacture of oxygen carrier materials from industrial grade raw materials. By now oxygen carriers have been produced mainly from pure substances in a lab scale. Within the FP7 Project SUCCESS two oxygen carrier materials have been produced in an industrial scale, using raw materials which are commercially available in large quantities. A spray dried material based on a perovskite structure with CLOU (Chemical looping with oxygen uncoupling) potential and a second material with copper as reactive material produced by impregnation.

Both oxygen carrier materials are tested in a 120 kW CLC pilot unit. The main fuel is natural gas from the local grid. Mixtures with natural gas, Propane and n-Pentane are also used as fuel to simulate the combustion of higher hydrocarbons. To complete the investigation of realistic operating conditions, the tolerance against Sulphur in the fuel is verified.

Both oxygen carriers show good fuel conversion performance with natural gas as fuel. Also after many cycles and hours of operation, both materials behave similar to the beginning. Only the impregnated oxygen carrier loses some copper at the very beginning of the tests. After some hours of operation, the copper amount on the particles stabilizes. The perovskite material has a homogeneous structure so attrition has no direct effect on the reactivity of the particles, since the composition does not change. Only the caused loss of specific inventory has an influence on fuel conversion. This dependency on the amount of oxygen carrier in the reactor system is noticeable for both materials.

Almost full fuel conversion is possible. Higher hydrocarbons as fuel are fully converted. The oxygen carriers show a drop in fuel conversion after the addition of $H_2S$. The copper based material is tested with Sulphur levels up to 2000 ppm in the fuel. The perovskite type oxygen carrier is tested with a fuel containing up to 3000 ppm.

The testing reported in this work shows that an up scaled production process is also capable to produce high performing oxygen carrier materials for CLC.

## 4.6 Oxygen carrier material testing at 150 kW (SINTEF ER)

**Chemical looping combustion of methane using copper oxide and calcium-manganite oxygen carriers in a 150 $kW_{th}$ reactor system for gaseous fuels**

Øyvind Langørgen[a], Inge Saanum[a], Nils Erland L. Haugen[a]

[a]*SINTEF Energy Research, Sem Sælands vei 11, 7034 Trondheim, Norway*

### Abstract

Chemical Looping Combustion (CLC) is a very promising CO2 capture technology where the oxygen needed for fuel oxidation is provided by oxygen carrier particles transporting oxygen from the air reactor to the fuel oxidation reactor. The fuel and air are not mixed so the exhaust from the fuel reactor contains only CO2 and water vapour and no further gas separation than water condensation is needed in order to get a pure CO2 effluent stream. The feasibility of this technology has already been proven and the technology is presently at the development stage at a scale up to about 1 $MW_{th}$.

SINTEF Energy Research and the Norwegian University of Science and Technology (NTNU) have designed and built a 150kWth reactor system which deals with many of the industrial and scale-up issues of the CLC technology. The reactor system is a double-loop circulating fluidized bed reactor system and key design features includes industrial applicability and scalability; flexibility with respect to oxygen carrier materials and excess air; and compactness for minimum oxygen carrier inventory. The reactor system is at present intended for gaseous fuels. The air and fuel reactors are 6 m tall of which the first 1 m is a conical bottom section. The remaining 5 m cylindrical sections have an internal diameter of 230 mm and 154 mm, respectively. Both reactors are working in the fast fluidization regime, which ensures that a high share of the reactor volume is effective in the conversion process. The two reactors are interconnected by pneumatically operated divided loop-seals. This allows recycling back a share of the solid particles within each reactor, thus increasing the effective residence time and control of the inventory. Fresh oxygen carrier can be fed during operation thanks to a feeding screw, and larger, agglomerated particles and bottom materials can be extracted by two water-cooled bottom extraction screws. Reactor cooling panels are mounted within the air reactor where most of the heat is released. The reactors do not have external heating so auto-thermal operation is required in order to keep the reactor temperatures at sufficient level for the oxidation and reduction reactions to be accomplished at necessary reaction rates.

In the present study two different oxygen carriers with different properties have been tested. First a copper based oxygen carrier formulation, made by impregnation using 15wt% CuO on a commercially available γ-alumina support. Next a calcium-manganite oxygen carrier (CMT) produced by spray drying was tested. Both materials have been produced within the EU FP7 project SUCCESS. The two oxygen carriers have almost identical size distribution with a median particle diameter d50 of 149 µm, whereas the particle densities are quite different. The bulk densities of the copper oxide and the calcium-manganite oxygen carriers are about 800 kg/m3 and 1600 kg/m3, respectively. The design values for the CLC reactor are particle size of about 100 µm and bulk density of about 1200 kg/m3. Especially the difference in density between the tested oxygen carriers and the design value may influence the performance.

The results using the cobber oxide oxygen carrier showed that at a fuel power of 140 kW the methane conversion was limited to about 90%, probably due to the low particle density compared with the design value. A derating of the fuel power was necessary and at 100 kW a methane conversion of up

to about 98% was achieved with an oxygen deficit of about 3% compared to the stoichiometric amount. The reactor temperatures were in the range 845°C to 858°C. At the same time, the specific fuel reactor inventory was just above 120 kg/MW, which is low compared to data found in the literature. The total active inventory in both reactors together was then 44 kg and the overall excess air ratio was about 1.2.

The calcium-manganite oxygen carrier has so far not performed that well, however, at time being only two separate test days have been finalised. Methane conversion reached only 73% in these tests (see Figure 1 below) with a fuel power of 115 kW. It should be noted that the $CO_2$ yield is almost equal to the methane conversion, meaning that almost no CO is going out the exhaust. The methane fuel is either converted fully to CO2 or not converted at all. The reactor temperatures were in the range 933-944°C and the air excess ratio 1.2. However, the specific fuel reactor inventory was as low as 101 kg/MW which may be a reason for the conversion not being higher. A second test point using somewhat higher specific FR inventory should improve the conversion but in the present test both the reactor temperatures and the total active inventory was reduced when performing this test. Therefore, the fuel conversion was in fact reduced.

The presentation will include more detailed evaluation and assessment of the results and operational implications. Improvements should be possible with some more optimisation of the reactor system operation, especially when using the more dense oxygen carrier.

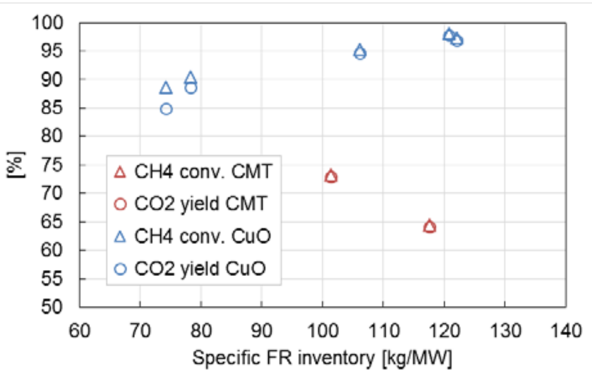


*Figure 1: Fuel conversion and CO2 yield vs. specific inventory*

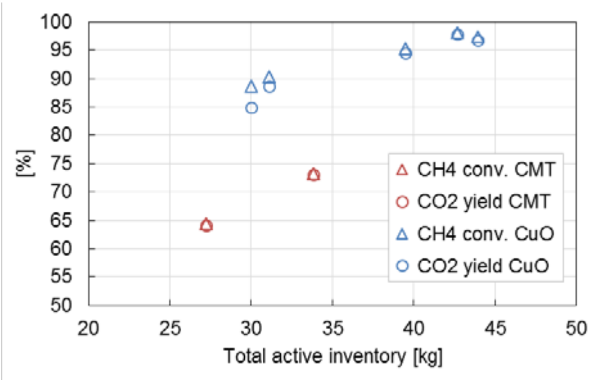


*Figure 2: Fuel conversion and CO2 yield vs.total active inventory*

## 4.7 Scale-up to 1 MW fuel power

### Operation of a 1 $MW_{th}$ chemical looping pilot plant with natural gas

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**Abstract**

Chemical looping combustion (CLC) is one of the most promising carbon capture and storage technologies. It is characterized by a low energy penalty, low carbon dioxide capture costs and low environmental impact. In comparison to a classic oxyfuel process, no air separation unit is required for chemical looping combustion. To prevent the contact between fuel and air, an oxygen carrier is used to transport the oxygen needed for fuel conversion. The process is operated in two interconnected circulating fluidized beds (CFB), referred to air reactor and fuel reactor, with a continuous loop of solid material between these reactors. The oxygen carrier is oxidized in the air reactor and reduced in the fuel reactor by means of gaseous or solid fuels. The CLC process for solid fuels using ilmenite as oxygen carrier was successfully demonstrated in the 1 $MW_{th}$ pilot plant at Technische Universität Darmstadt in the recent years. Within the SUCCESS project, CLC of natural gas was tested in the 1 $MW_{th}$ scale.

To enable the pilot plant for gaseous fuel operation, some adaptations of the design were made (cf. Figure 1). A flue gas recirculation was installed to simulate real conditions of a full scale CLC plant and to simplify operation. Natural gas was compressed to a pressure level of 2.5 bar(g) by a new natural gas compressor (not shown in Figure 1) and was introduced to the fuel reactor at two different heights. The secondary fluidization of the fuel reactor should enable both a high solids inventory of the fuel reactor and a high solids circulation between fuel and air reactor. Additional measurement equipment was used to determine dry gas concentrations and moisture.

A CLOU (Chemical Looping with Oxygen Uncoupling) oxygen carrier (Ca-Mg-Ti-Mn-oxide) that had been developed within the SUCCESS project was used for CLC tests. Stable CLC conditions were reached for ~ 50 h during tests with the CLOU material. The $CO_2$ yield was in the range of 80 %. The pilot was operated autothermally for a short period of time. The flue gas recirculation worked excellently, and the specific inventory was increased by the usage of the secondary fluidization. Pure oxygen was introduced to the post oxidation chamber (POC), and the hot flue gas was cooled directly downstream by a water injection. Almost full conversion of gases like $CH_4$, CO and $H_2$ was achieved in the POC for the whole test duration. Many samples were taken from fuel and air reactors to investigate the evolution of the material and the solids circulation. Attrition was determined from the fine fraction of samples from the fabric filters. Attrition of the material was in the range of 0.2 - 0.4 wt.-% $h^{-1}$.

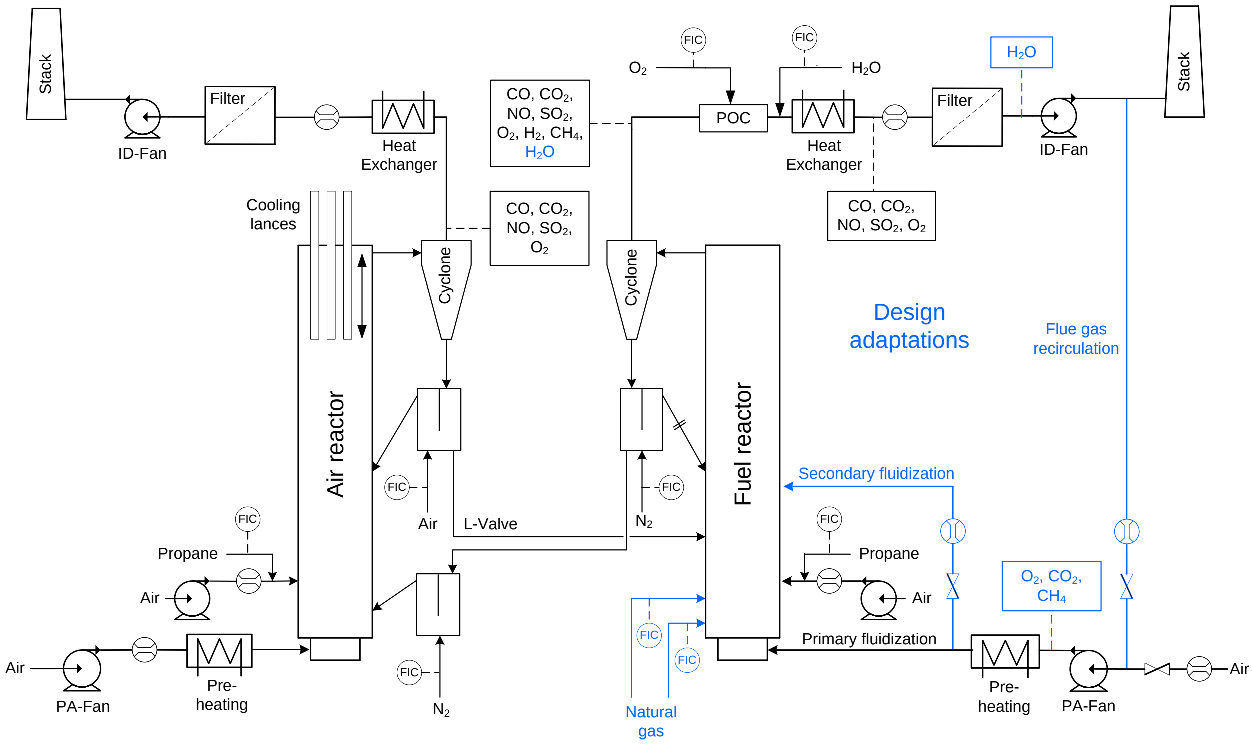


*Figure 1: Simplified scheme of the 1 $MW_{th}$ chemical looping pilot plant (modifications for test campaigns with natural gas as fuel shown in blue).*

## 4.8 3D-Modelling results

**Coupling between gas-solid reaction modeling and CFD multiphase approach for 3D numerical simulation of a 120 kWth CLC unit and comparison with experimental data**

Ziad Hamidouche[a], Enrica Masi[a], Pascal Fede[a], Hervé Neau[a], Olivier Simonin[a], Karl Mayer[b], Stefan Penthor[b] and Juan Adanez[c]

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*[b]TU Wien, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria*
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**Abstract**

In this work, three-dimensional unsteady numerical simulations of a Chemical Looping Combustion (CLC) plant are performed and analyzed. The pilot is a 120kWth unit located at Vienna University of Technology (TU WIEN), using natural gas as a fuel and, for the selected operating point, perovskite as oxygen carrier. The pilot is a dual circulation fluidized bed composed by an air reactor (AR) and a fuel reactor (FR) connected each other by upper/lower loop seals ensuring solid circulation and preventing gas mixing between the reactors. Loop seals are fluidized by steam while air and fuel reactors are fluidized by air and natural gas respectively. In the fuel reactor, an internal solid circulation may occur thanks to an internal loop seal. In the experiments, different oxygen carriers and operating points have been investigated [1]. In the numerical simulations, only one oxygen carrier at one operating point is considered.

Unsteady three dimensional numerical simulations are performed using the Eulerian N-fluid modeling approach for fluid-particle turbulent polydispersed reactive flows implemented in NEPTUNE_CFD V1.08@Tlse version by IMFT (see, e.g., Ref. [2]). The Euler-Euler approach computes both the gas and the solid phases in an Eulerian framework accounting for specific closures in order to model interphase mass, momentum and energy transfers. Reduction and oxidation gas-solid reactions are modeled by means of a grain model (shrinking core model) accounting for both the competing mechanisms of chemical reaction at the particle surface and gaseous diffusion through the particle layer. Kinetics parameters and reaction mechanisms are provided by the Instituto de Carboquímica (ICB-CSIC) [3]. In the numerical simulations, the δ parameter in the perovskite formula, $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$, is assumed to be constant and set to 0.1. The numerical configuration does not include neither internal nor upper loop seals and cyclones. Their effects are accounted for in the simulations by appropriate boundary conditions. The entire domain is meshed using a grid involving 1.723 million cells. Results obtained from the numerical simulations are compared with the experimental measurements and analyzed in order to gain insight in the local behavior of the CLC system. As an example, Figure (1) shows pressure-drop profiles along the axial direction in both the fuel and the air reactors. The main features of the two reactors (dense versus circulating behavior) are reproduced by the numerical simulation. Figure (2) shows the instantaneous solid mass in each reactor and the solid mass flow rate at the AR outlet compared with the experiments. Species molar-fraction predictions at the reactor exit are depicted in Figure (3).

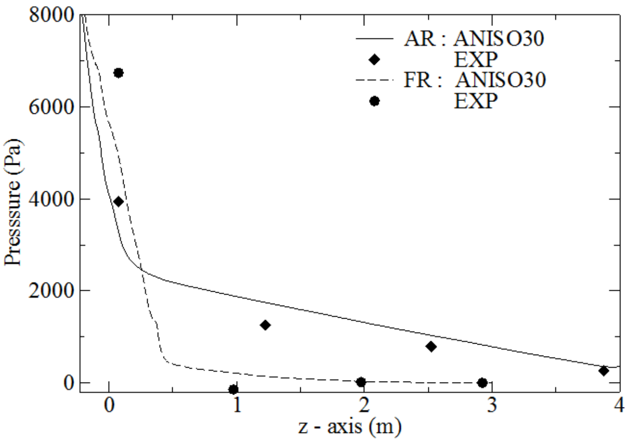

*Figure 1: Mean pressure drop profiles in FR and AR*

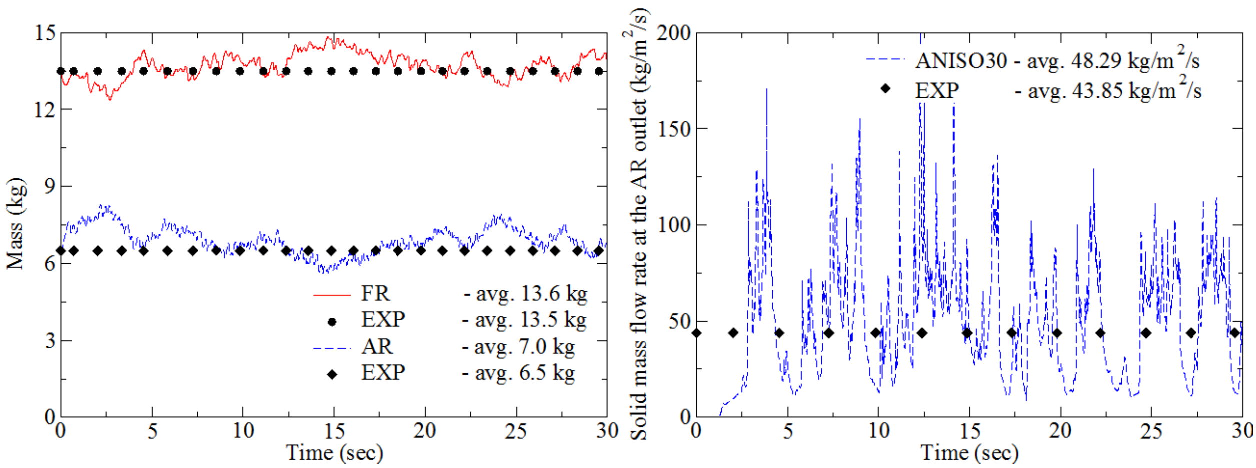

*Figure 2: Time evolution of the solid mass in AR and FR (left); solid mass flow rate at the AR outlet (right)*

Globally, numerical results are found in good agreement with experimental measurements. The theoretical and numerical tool developed in this work will be used for design upgrade recommendation in the stage of scaling-up from pilot to industrial facilities.

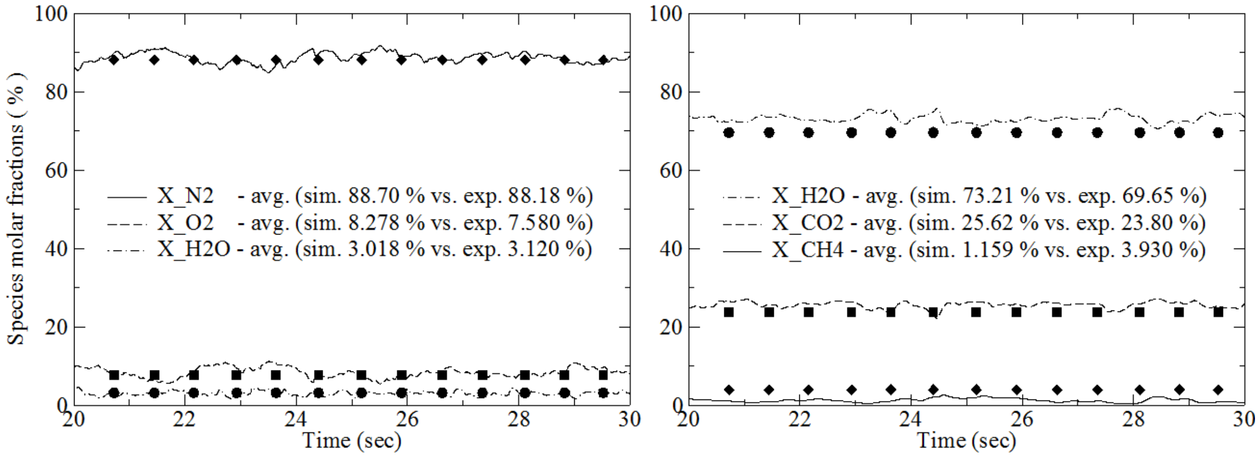


*Figure 3: Instantaneous and mean molar fractions of the gaseous species leaving the AR (left) and the FR (right)*

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## 4.9 Health and safety assessment, life cycle analysis and recycle options

### Scale-Up of oxygen Carrier for Chemical-looping combustion using Environmentally SuStainable materials (SUCCESS) – Health & safety assessment, Life Cycle Analysis and recycling options


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**Abstract**

The oxygen carriers (OCs) used in the project for chemical looping combustion (CLC) are complex metal-oxides which are fluid-like due to the small particles and spherical shape. We investigated the environmental impact, life cycle at steam generation, and recovery routes for 2 types of OCs: (i) Cu-impregnated OCs and (ii) spraydried perovskite-type Mn-ore based OCs.

It is of high importance to study the safety of workers and the environment at an early stage of process development. Effects of the OCs on the aquatic and terrestrial environment were examined in ecotoxicity tests. Results indicate that the water soluble fraction (WSF) of the Cu-based OC is very toxic to

algae (figure 1), so OC release to surface water should be avoided. Effects on workers who are exposed via inhalation were examined with *in vitro* tests, which showed that dust particles that were generated by Mn-based OC (called C-28) have the potency to initiate allergic reactions (figure 2), so dust generation or exposure to dust should be avoided.

Figure 1: toxicity of Cu-OC to algae

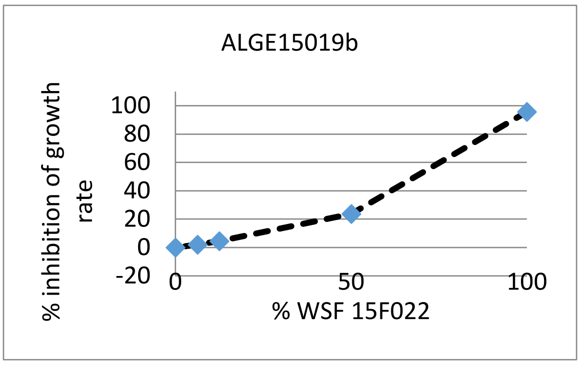
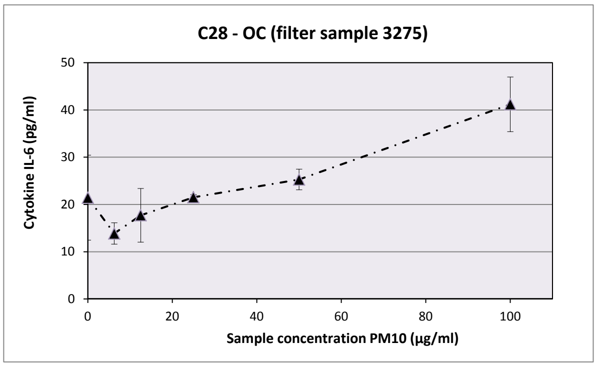



Figure 2: *in vitro* toxicity of Mn-OC (C28)




The release of OCs in a research environment was simulated by pouring OCs in the hopper of a vibrating feeder followed by transport across a conveying chute and dropping onto a stainless plate, simulating the handling of intensely used metal-oxide particles. Comparison of air concentrations with occupational exposure limits (OELs) showed that respiratory protection is recommended during exposure to Mn-OC dust. For the industrial setting, the Fluid Catalytic Cracking (FCC) process was used as a reference to define six exposure scenarios for the workers, of which 'spent catalyst unloading' retrieved the highest exposure levels. The scenarios were assessed in the Advanced REACH Tool (ART). The two most relevant exposures are to Mn and to Cu, for which the calculated exposure are only 10% and 2% respectively of the OEL. Hence there is no need for additional risk management measures.

Recovery routes for the spent material were investigated. Cu-OC has some deactivation generating small amounts of fines containing CuO and CuAlO2. Fines separated by cyclones (cut-off size: 50 µm) from a 10 kWh CLC prototype were used as raw material in an acid leaching process to recover Cu. Recovering efficiencies of ~95 % were obtained by $HNO_3$ leaching and the final products were a $Cu(NO_3)_2$ containing eluate and a solid residue. The eluates could be used for the preparation of new OCs by impregnation. We have shown that this impregnation route can apply the coarse fraction of spent OCs as support. The obtained new OCs exhibited high reactivity for reduction and oxidation reactions as well as adequate physical and chemical properties to be used in a CLC plant. Furthermore, the fine fraction of the solid residue from the leaching experiments was processed into high-strength ceramic spheres. The obtained materials can be used in the production of milling balls or fillers. The proposed recovery and recycle processes largely decrease the need for natural primary resources (Cu and Al2O3) as well as provide novel recycling paths for the Cu-OC waste generated in the CLC process.

The spray-dried Mn-OCs do not contain high amounts of valuable metals. Therefore, closed-loop recycle options for these OCs at their end-of-life were investigated. Research was performed on the reprocessing of spent spraydried OCs after milling as new spraydried OCs. Preliminary tests of the re-processed OCs showed similar reactivities as fresh OCs.

Life cycle assessment (LCA) can be applied to study the effect of CLC on climate change and other environmental issues. In the LCA, the environmental impacts associated with infrastructure and processes of steam production in full-scale natural gas CLC steam plants are analysed. Two types of plants are selected: 700 MW plants that generate electricity and 100 MW plants that produce steam only. As a next step, their impact is compared to that of amine-based post-combustion capture steam plants of comparable size.

The full life cycle of the power plants is considered, including the construction, operation and disassembly at the end of life. For each step of the life cycle, all inputs (resources and energy consumed) and outputs (emissions and waste) are quantified and their potential effects on the environment, human health and resource depletion are determined. The operation of the plants includes the use of OCs, which are analysed starting from their production and ending with their waste treatment. Data on the toxicity of OCs is obtained from the environmental impact assessment performed in SUCCESS, and is incorporated in the selected LCA method.

The results show that the environmental impact of power generation is mainly determined by the operation of the plant. Especially the use of natural gas has a major influence on the results. The transport and storage of the compressed $CO_2$ output also have a fairly important contribution to the environmental impact of the steam plants. For the reference plants, the direct emissions from the steam production process have a large contribution to some impact categories. Since the consumption of natural gas is one of the main determinants of the environmental impact, the efficiency of the plants has a major effect on the results. Further work to improve the efficiency of the CLC plants is thus needed to reduce their environmental impact and make them the best option for power generation from gaseous fuels from an environmental perspective.

## 4.10 Techno-economic evaluation of CLC steam generation

**Chemical looping combustion for power and steam generation from natural gas – process arrangements and expectable performance**

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**ABSTRACT**

Chemical Looping Combustion (CLC) offers the possibility for efficient fuel conversion with inherent $CO_2$ capture and is expected to significantly reduce the energy penalty associated with $CO_2$ capture processes. Feasibility of the concept has been shown and studied thoroughly in lab experiments whereas the potential for power generation at large scale will depend on the process configuration. In power generation from natural gas fuelled power stations, modern Gas Turbine Combined Cycles (GTCC) are usually very efficient processes and electric efficiencies up to 60% are reached without CO2 capture [1]. GTCC processes with absorption based post combustion $CO_2$ capture typically show overall net efficiencies of 51-52%$_{LHV}$ at full load when 90% of $CO_2$ is captured and compressed to 110 bar [2]. It is the reference scenario that CLC of natural gas for power production will be compared to. Iyer et al. state that the penalty for $CO_2$ separation from GTCC plants via PCC will account for 6.7-7.4% [3] Electric efficiencies of 42-43%$_{LHV}$ are observed for natural gas fired power stations equipped with pre-combustion $CO_2$ capture units [2]. Different scenarios for competitive power generation from CLC of

natural gas have been assessed via process simulation for atmospheric reactors as well as for pressurized reactors. Process design is shown and discussed based on net electric efficiencies.

For atmospheric reactors, real net efficiencies around 40% are obtained for single pressure level/single reheat steam generator and delivery of $CO_2$ at ambient pressure. Introducing additional pressure levels might improve overall processes efficiency and real net efficiencies to more than 40% can be expected when more sophisticated steam cycle designs are applied. This shows that, when atmospheric fluidized bed reactors are used, the electric efficiency of a CLC power station will be in the range of solid fuel power stations but not in the range of natural gas fired power stations. Pressurized chemical looping combustion (CLC) was studied with regard to its potential for power generation from gaseous fuels, such as natural gas. A process simulation model was set up for a simplified gas turbine combined cycle (GTCC) around a pressurized CLC reactor system and studied with respect to process parameters influencing electric efficiency. The process model is based on typical large scale GTCC arrangements with a gas turbine topping cycle and a heat recovery steam generator unit (HRSG). The results are compared to conventional GTCC process with similar arrangement and process parameters. It was found that the CLC process comes along with considerable technological limitations for the efficiency of the combined cycle: (i) turbine inlet temperature is limited by the oxygen carrier material, (ii) pressure drop of CLC AR path increases the required air compression work, and (iii) the requirement for low pressure steam for gas-sealing between air reactor and fuel reactor reduces the efficiency of the steam cycle. These effects limit the achievable net electric efficiency to values below 45%, which is similar to what could be reached with atmospheric pressure CLC in a conventional steam cycle power plant arrangement (e.g. Benson-type steam generator). The gas turbine inlet temperature (TIT) was identified as the greatest limitation to the process, the pressure ratio has to be reduced accordingly to maintain sufficient exhaust gas temperatures in the HRSG, which limits the efficiency potential of the gas turbine. As a conclusion, when it comes to power generation from gaseous fuels, these limitations will need to be resolved to make CLC technology competitive with conventional GTCC power plants combined with post combustion $CO_2$ capture technologies. Concerning steam generation for industrial applications such as EOR or pulp and paper production, no significant limitations were identified which makes CLC a highly promising alternative to conventional combustion in this field.

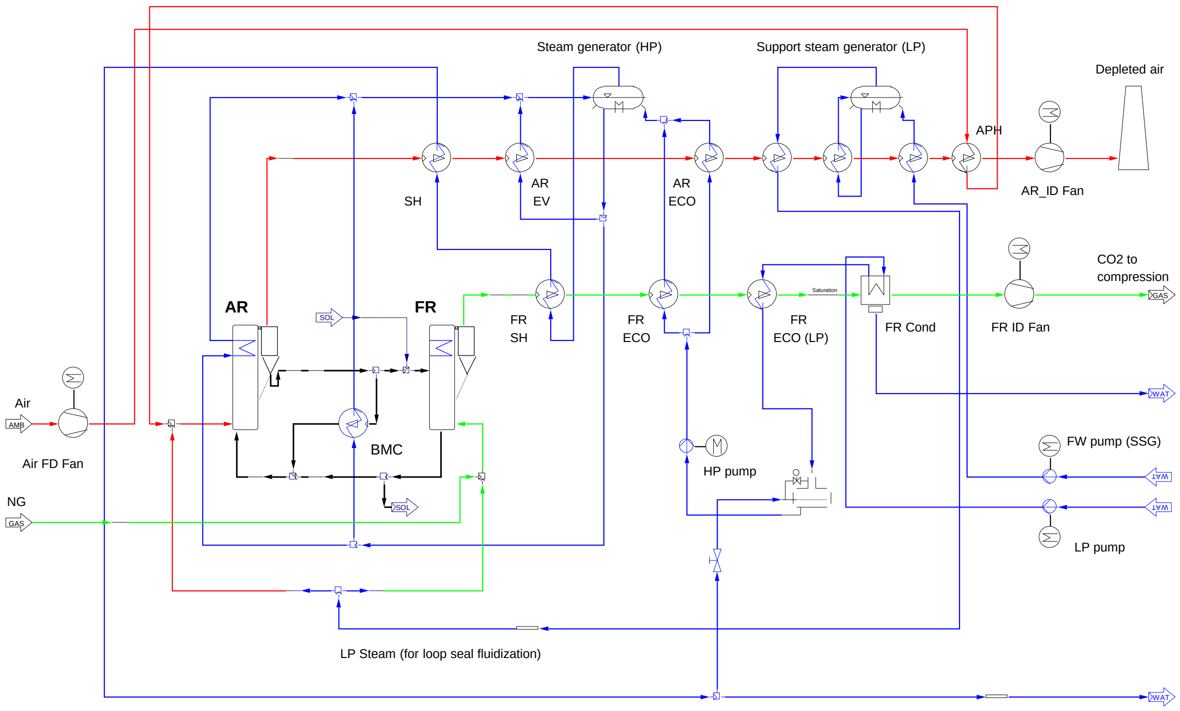


Figure 1: Flowsheet model of an atmospheric CLC plant for industrial steam generation

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