CLEEN
Cluster for Energy and Environment

Research Report D317
Helsinki 2015

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D317:Development of oxygen carrier synthesis methods and characterization of oxygen carriers applicable for solid fuels

ccsp
Carbon Capture and Storage Program

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Report Title: D317: Development of oxygen carrier synthesis methods and characterization of oxygen carriers applicable for solid fuels

Key words: CLC, chemical looping, oxygen carrier

Abstract

In order to decrease carbon dioxide release to atmosphere chemical loop combustion (CLC) has been intensely developed for several years. In CLC fuel is burned in a power plant instead of air using solid oxides to carry the oxygen. In this way CO_2 can be separated from the effluent gas more easy than in conventional combustion. The oxygen carriers must have large enough oxygen capacity, reactivity with the fuel, free flowing characters, together with mechanical and chemical resistance. Oxygen carriers were tested in fluidized bed with different fuels. The oxygen carrier was prepared by mixing active NiO and inert Al_2O_3 using bead mill and spray dryer to form large enough granules for fluidized bed testing. Two main characteristics tested were reactivity and mechanical resistance in fluidization. Oxygen carriers were studied before and after testing. Granules crushing strength was tested before testing sintered at different temperatures.

Jyväskylä, 9th October 2015

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1 Introduction

Chemical-looping combustion (CLC) is a technology with the potential of reducing the costs and energy penalty of CCS. Chemical-looping combustion is based on two reactions which take place at two different sections and in turns. These reactions are oxidation and reduction reactions. Usually the sections are called the air reactor and the fuel reactor.

The oxygen carrier is the most essential component of the CLC process. It transfers heat and oxygen at the process between reactors. Many design issues depend on the properties of the oxygen carrier. Important properties of the oxygen carrier are the oxygen carrying capacity and reactivity. Circulation rate is highly dependent on these characteristics.

For overall suitability of oxygen carrier good durability against attrition and fragmentation are needed. These characteristics are related to needed make-up of oxygen carrier and thus variable cost of process.

2 Objective

The objective of the study was to design and modify existing testing bench scale device to be more suitable for reliable oxygen carrier testing. This included possibility to determine and evaluate strength, durability of oxygen carrier and long term reactivity. Oxygen carriers were tested to produce more knowledge and evaluate existing testing readiness.

3 Content and methods

The assessment was carried out by design of testing device modification, acquisition of needed parts and testing of existing or manufactured oxygen carriers.

Methods:

- Oxygen carriers were tested at bench scale test rig in batch-wise mode. This contained gaseous and solid fuels.
- Attrition and fragmentation rate was evaluated from the particle sizes before and after the testing. Evaluation and estimation of oxygen carrier suitability for the process.

4 Oxygen carriers and bench scale device

NiO was selected for oxygen carrier to present reference oxygen carrier from the literature [Jerndal et al., 2009; 2010]. The oxygen carrier was prepared by mixing active NiO 40wt% and inert Al_2O_3 60 wt% using bead mill and spray dryer to form large enough granules for fluidized bed testing.

Transition metal oxides are most often considered to have suitable properties to act as oxygen carriers. These active materials must be mixed with some inert material in order to gain resistance against chemical and thermal cycling in highly erosive environment.

NiO 40% Al_2O_3 60% was sintered at different temperatures to increase the crushing strength of the granules. The strength was measured compressing a bed of granules in such way that the granule structure was disintegrated (***Figure*** 1). 1400 ºC was the maximum temperature that the sintering was able to be done still having loose powder.

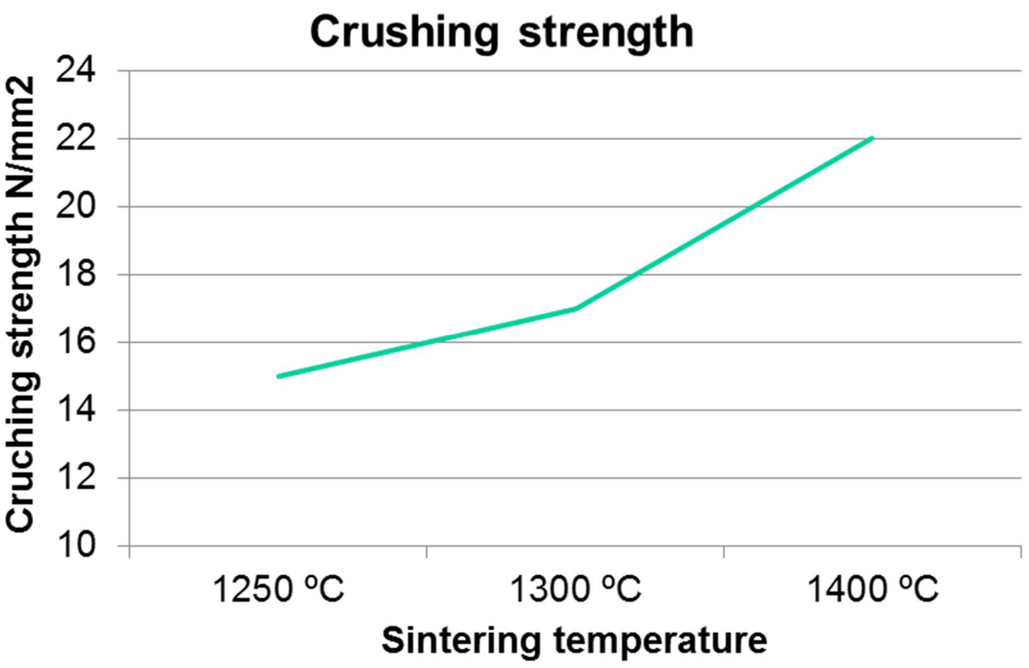

Figure 1. Measured crushing strength of NiO-based oxygen carrier, before fluidization for different sintering temperatures.

SEM pictures (***Figure 2*** and Figure 3) were taken from the constructed oxygen carriers to define surface structure of particles. These pictures were visually inspected before and after testing.

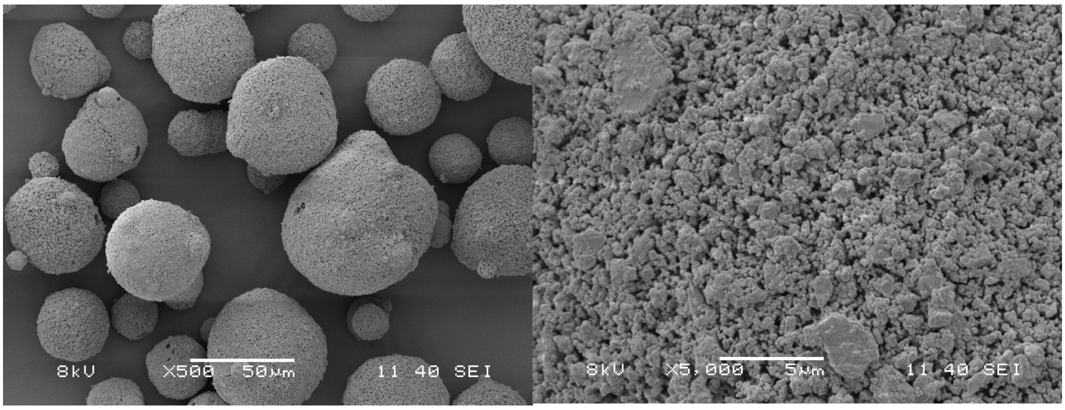

Figure 2**.** NiO-Al_2O_3 spray dried oxygen carrier, sintered at 1400 ºC for 6 hour. SEM picture before testing the oxygen carrier.

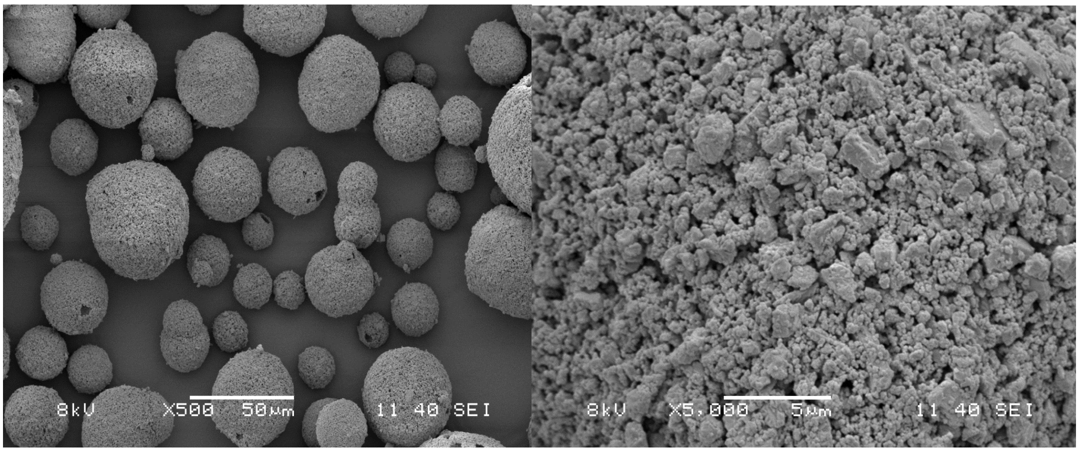

Figure 3. NiO-Al_2O_3 spray dried oxygen carrier, sintered at 1400 ºC for 6 hour. Tested in fluidized bed reactor using 8% CO as a fuel, volume flow of 1Nl/min. It can be seen compared to figure above that granule structure is still similar, granules intact and round in shape.

These oxygen carriers were tested at bench scale combustion unit (Figure 4). Combustion unit have been earlier used for fuel reactivity test. Bench scale unit can be operated both bubbling and circulation fluidization modes.

Figure 4 Bench scale fluidized bed combustion unit.

5 Results

Several different cycling were made during testing. NiO based oxygen carrier were tested with syngas and solid fuel. Solid fuel was chosen to be South African coal, due low sulphur content. Sulphur is known to decrease oxygen carrier activity [Hossain et al., 2008].

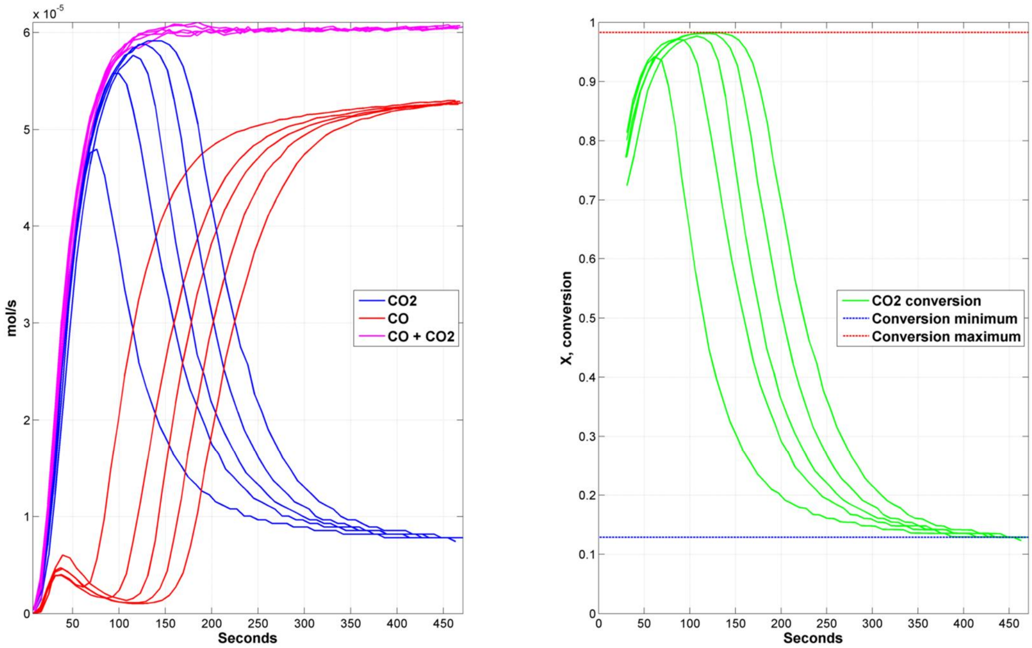

Figure 5. Five first batch-wise cycles of nickel based oxygen carrier: molar flows of main gaseous species (on left) and CO_2 conversion (on right)

NiO oxygen carrier particles increase their activity after multiple reduction-oxidation cycles. From Figure 5 it can be seen that oxygen release of oxygen carrier is improved during five reduction cycles with carbon monoxide at temperature of 925ºC. CO2 conversion graph shows that capacity to release oxygen also increases. This may be caused of micro-structure changes at oxygen carrier during cycles.

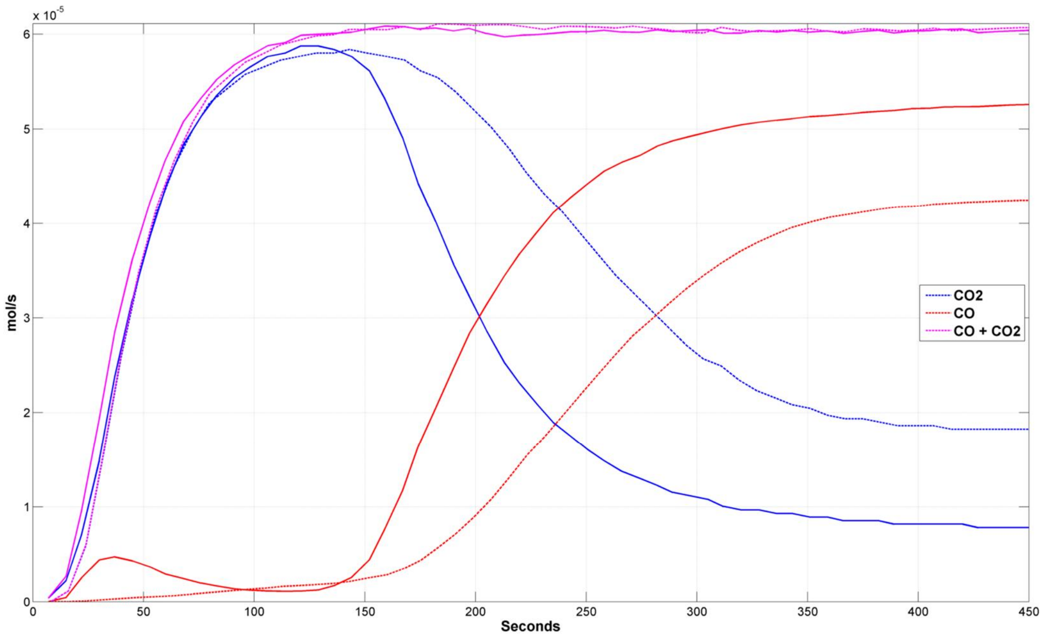

Figure 6. Nickel based oxygen carrier at two different temperatures with carbon monoxide.

Figure 6 shows effect of temperature to carbon monoxide conversion of NiO. Solid line is reduction phase of oxygen carrier at temperature of 925ºC and dotted/pale line is at temperature of 1000ºC. Higher temperature is more favourable for reactivity of oxygen carrier.

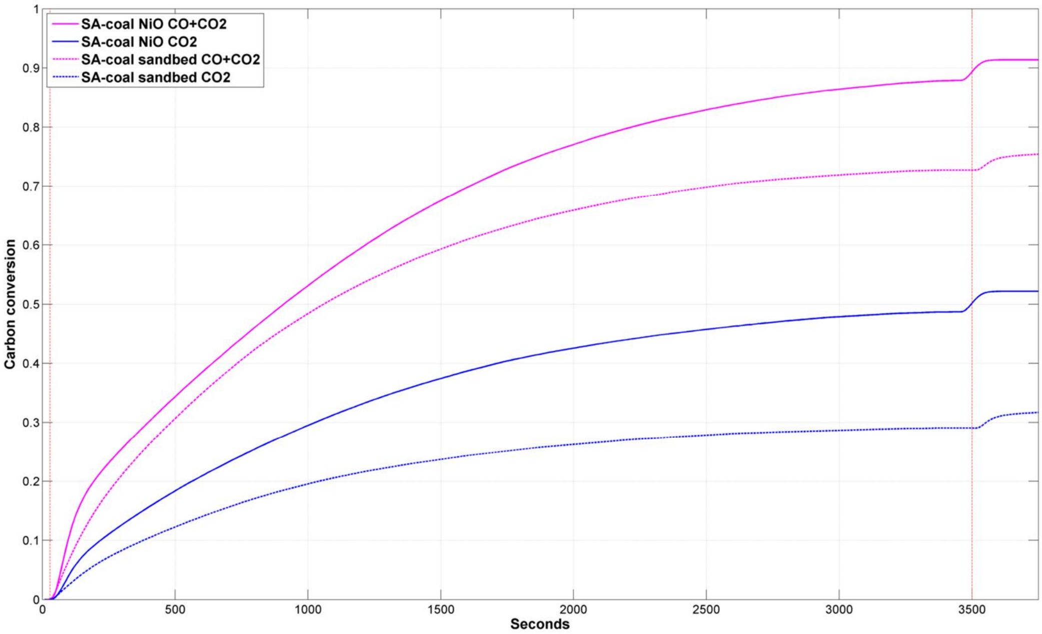

Figure 7. Nickel based oxygen carrier tested with South African coal and comparison to inert sand bed.

NiO oxygen carrier were tested with South African coal, after testing with gaseous fuels. Particle diameter of coal batch was about 2 mm and total mass of fuel impulse was 0.5 g. Fluidization gas was nitrogen-steam mixture with ratio of 50%-50%. Steam was used to increase gasification of coal, because solid fuel and solid oxygen carrier tends to react slowly. Figure 7 shows carbon conversion calculated from gas composition measured from the flue gas. Dotted/pale line is with same fuel, but with sand bed which is not reactive or oxidated. Red dotted lines show insert of batch and oxidation of carbon residue. Comparison shows increase of carbon conversion to carbon dioxide with oxygen carrier. Nevertheless reactions with solid fuel are slow and full conversion is hard to obtain.

From Figure 8 it can be seen that there was no clear difference on particle size of oxygen carrier before and after tests. This was also confirmed in fluidization tests as no measurable weight loss was noted. Amount of eroded particles during the tests was insignificant. These are still initial test results and may not present real behavior at the utility scale.

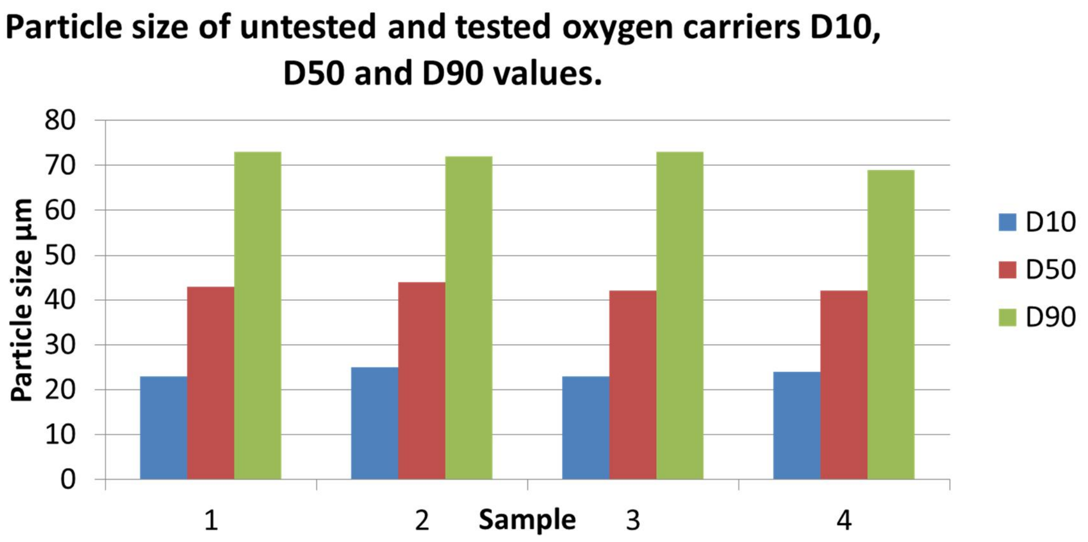

Figure 8. Characteristic particle sizes of oxygen carriers: 1 before tests and 2-4 after tests.

6 Discussion

Testing of oxygen carriers with existing device was not fully successful. Good process conditions were not met in the sense of combustion. Major part of results contained more gasification than combustion itself. Also reactivity with solid fuel was low, which can be caused by selection of active material of oxygen carrier (NiO) or too high sintering temperature.

7 Summary

NiO-Al_2O_3 oxygen carrier was produced by spray drying. Crushing strength of oxygen carrier was tested and chemical reactivity was evaluated by batch-wise fluidized bed tests. Tested oxygen carriers were found to resist mechanical stress of fluidized bed without structural changes. With solid fuel, some reactivity was found using steam as agent to increase carbon gasification. Anyhow, combustion results were unsuccessful due to partly improper test device and unreactive oxygen carriers. In order to test this kind of materials more profoundly longer tests with large number of cycles should be done. More comprehensive testing would need continuous testing procedure, not only batch-wise testing.

Fluidized bed combustors in industrial size need coarser granules which could be done using considerably larger spray dryer. Constructions of such particles are not available at the moment in VTT.

Part of these results has been presented earlier at Partec conference, [Lagerbom, 2013].

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