Evaluation of manganese-silica oxides as oxygen carrier for Chemical-Looping Combustion at high temperatures

Master of Science Thesis

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Contents

1. Introduction ............................................................................................................................................ 1
   1.1. Global warming and the greenhouse effect ....................................................................................... 1
   1.2. Combustion technology with CO₂ capture ....................................................................................... 2
   1.3. Chemical Looping Combustion (CLC) ............................................................................................ 3
   1.4. Chemical looping with oxygen uncoupling ...................................................................................... 4
   1.5. Oxygen carriers .............................................................................................................................. 5
   1.5.1. Mn oxides oxygen carriers .......................................................................................................... 6
   1.6. Objective ....................................................................................................................................... 9
2. Experimental ............................................................................................................................................ 10
   2.1. Experimental setup ......................................................................................................................... 10
   2.2. Manganese silicate particles in this study ....................................................................................... 11
   2.3. Reactivity test of manganese silicate oxygen carrier ...................................................................... 11
   2.4. Data Analysis .................................................................................................................................. 13
3. Results and discussion ....................................................................................................................... 14
   3.1. Reactivity towards syngas ............................................................................................................... 14
   3.2. Reactivity towards CH₄ ................................................................................................................... 15
   3.3. CLOU property after oxidation by 5% O₂ ..................................................................................... 19
   3.4. CLOU property after oxidation by air ............................................................................................ 21
   3.5. CLOU behavior in multiple cycles ................................................................................................. 24
   3.6. M5 phase analysis by XRD .......................................................................................................... 25
4. Conclusions ............................................................................................................................................ 26
5. Acknowledgements ............................................................................................................................. 27
References ................................................................................................................................................ 28
1. Introduction

Nowadays, it is not a novelty to state that a new energy era is coming. Oil reserves are predicted to be depleted in decades. Thus, an important challenge is headed to scientist community to find alternative sustainable energy sources. Many factors, such as economic viability, environmental impact or transportability need to be taken into consideration in research. Until feasible and completely sustainable new sources of energy would have been developed, several strategies must be applied to reduce serious negative effects on the earth caused by combustion of fossil fuels. Fossil fuel combustion emits thousands of tons of CO$_2$ every year and will still be the main energy source in foreseeable decades. Under such circumstances, CO$_2$ capture and storage is one of the most important strategies demanding to be carried out.

1.1. Global warming and the greenhouse effect

Global warming is a phenomenon that the average global temperature increases due to anthropogenic activities. The top ten warmest years since global temperature has been recorded all occur during 1997-2008 [1]. Further, it is predicted that the rising of average temperature will accelerate in 21th century. Although irreversible changes have been done to earth’s ecosystem, worse situations can be avoided if proper actions are taken, for instance, mitigation and adaptation strategies. [2] Mitigation against climate change aim at decreasing anthropogenic emission of greenhouse gases, thus to suppress the rate of long-term environmental deterioration. To already existing climate change, adaptation strategy which acts to reduce potential damages caused by global warming is important. Mitigation and adaptation are considered as a medium-term solution, and technologies focusing on removing greenhouse gas emissions can play a significant role against global warming. Developing renewable and sustainable energy sources is another big part in mitigation strategy.

Greenhouse effect is the main reason for global warming. Greenhouse effect is a process where thermal radiation from earth is absorbed, and then re-radiated in all directions by atmospheric greenhouse gases. Since a part of this re-radiation is back towards earth, energy is transferred to the lower atmosphere and earth surface in form of heat. As a result, the average temperature on earth is higher than it would be if no greenhouse gases exist in the atmosphere. [3]With the increasing concentration of greenhouse gases (GHG) in atmosphere, the global warming effect is more and more severe in the past decades. Primary GHG are water vapor, carbon dioxide, CH$_4$, nitrous oxide and ozone [4]. Among them, CO$_2$ has the greatest greenhouse effect. The emitted CO$_2$ has the highest radioactive forcing and a lifetime over hundreds of years. What
worse is that CO$_2$ concentration in atmosphere keeps increasing since industry revolution age. The level of CO$_2$ has far beyond what ecosystem can balance by natural processes. In preindustrial era, CO$_2$ concentration was 280ppm. Nowadays, it is approximately 390 ppm in the atmosphere [5]. Burning of fossil fuels and deforestation are the main anthropogenic acts responsible for this rise. According to U.S. EPA (Environmental Protection Agency), the major GHG contribution to end-user sector is fossil fuel combustion industry and transportation [6]. So, reducing of CO$_2$ emissions from fossil fuel combustion is crucial.

### 1.2. Combustion technology with CO$_2$ capture

To depress the amount of CO$_2$ emitted into atmosphere meanwhile still utilize fossil fuels as an energy source, CO$_2$ capture and storage (CCS) is proposed. In CCS process, CO$_2$ is first separated from other gases, then liquefied to facilitate transportation and stored. The first step in CCS, i.e. capture, can be practical at various industrial carbon dioxide producing sites. Condensed CO$_2$ can be stored in geological resources, for instance under the sea and in depleted oil fields. The captured CO$_2$ can also be used in other industrial processes, which is then another concept rather than CCS.

Considering CO$_2$ capturing, three technologies have been often discussed. They are: post-combustion, pre-combustion and oxy-fuel combustion. Though post-combustion and pre-combustion have been estimated economically feasible under specific conditions, neither of them have reached industrial level yet. On the other hand, oxy-fuel combustion is still under research phase. [7][8]

**Post-combustion**: the concept of this technology is to separate CO$_2$ from combustion exhaust gases. Calcium oxide looping [9] and chemical absorption by amines (e.g.: monoethanolamine (MEA), methyldiethanolamine (MDEA) or ammonia-base solutions) [10] are two widely studied processes for CO$_2$ separation. Other methods, such as physical adsorption, cryogenic distillation or membranes are also under development.

**Pre-combustion**: in pre-combustion technology, primary fuel mixed with steam and air (or oxygen) is processed in a reactor to produce carbon monoxide and hydrogen (syngas). In a second reactor (shifting reactor), CO reacts with steam producing H$_2$ and CO$_2$. In the last step, CO$_2$ is separated from hydrogen which is used in CO$_2$ free combustion. [11]

**Oxy-fuel combustion**: in this technology, O$_2$ is separated from air and mixed with CO$_2$ which is produced from combustion. Fossil fuels are burnt in O$_2$/CO$_2$ mixture instead of pure O$_2$ to avoid excessive heat release. The exhaust stream then consists of only steam and CO$_2$. CO$_2$ is typically about 90% and recirculated to the combustor mixing with O$_2$ after steam condensation. In oxy-fuel combustion, formation of NO$_x$ is reduced by around 70-80% compared with normal combustion. On the other hand, SO$_x$ may cause problems, such as high-temperature corrosion.
on boilers’ surface. So SO\textsubscript{x} needs to be removed from the recycle CO\textsubscript{2} stream.\ [12] Oxy-fuel combustion technique is chiefly used in new-generation power plants with water-vapor cycles or gas turbines.

From economy point of view, a previous research estimated that applying CO\textsubscript{2} capture to combustion would involve an increase of electricity generation about 0.01-0.05 U.S.$ per kWh, depending on the kind of fuel, the specific technology, the location and the national circumstances\ [13]. Since many variables affect electricity price (e.g. fluctuant evolution of fossil fuel price, costs added by CO\textsubscript{2} capture, price reductions due to better CH\textsubscript{4} extraction, etc.) a comprehensive economy study may be of great interest. Nevertheless, it is expected that building new power plants including CO\textsubscript{2} capture technologies would obtain higher efficiency of electricity generation and lower costs compared to adapting old ones.

1.3. Chemical Looping Combustion (CLC)

A promising innovative technology, Chemical Looping Combustion (CLC) is under development. With this technology, the O\textsubscript{2} in combustion air is partly removed by oxidation of a transition metal oxide (an oxygen carrier) which is reduced by fuel afterwards. In this way, the combustion needed O\textsubscript{2} is transferred to fuels without the necessary of gas separation.

Chemical Looping Combustion is not a new concept. In 1954, Gilliland patented “Production of industrial gas comprising carbon monoxide and hydrogen”. This patent described a method using a metal as an oxygen carrier, which was oxidized in air, and reacts with hydrocarbon in fluidizing conditions to produce syngas. This can be regarded as the first on paper record of CLC concept. Between 1950 and 1954, Gilliland, together with Lewis, published an article titled “Production of pure carbon dioxide” using the same method. Richter and Knoche proposed that CLC process can be beneficial in combustion with the advantage of increased combustion efficiency.\ [14] Not until a thermodynamic study carried out by Ishida did the mentioned above process start to be identified as it is currently known as CLC. Seven years later, Ishida proposed CLC as a technique to capture CO\textsubscript{2}.\ [15] In the last decade, academic publications related to CLC have exponentially increased. And lab scale CLC unit has scaled up to 1 MW\textsubscript{th} in Damstadt, Germany.

A Chemical Looping Combustion unit consists of two fluidized bed reactors (an air reactor and a fuel reactor) where a metal oxide is used as an oxygen carrier to transfer O\textsubscript{2} from the air reactor (AR) to the fuel reactor (FR). The oxygen carrier is oxidized in the AR, and then circulated to the FR where it is reduced giving O\textsubscript{2} to fuel. The reduced oxygen carrier then returns to the AR and a new cycle continues. Main reactions that take place in a CLC cycle are:

\[
C_nH_{2m} + (2n+m)Me_xO_y \leftrightarrow nCO_2 + mH_2O + (2n+m)Me_{x-1}O_y \quad (FR) \quad (1)
\]
As seen from eq.(1), the outlet stream from FR is a mixture of steam and CO\textsubscript{2} if fully conversion is obtained. After steam condensation, pure CO\textsubscript{2} is ready for compression, transportation and storage.

By adding eq.(1) and eq.(2), one can find that the heat generated by CLC is the same as by normal combustion. So there is no energy loss involved in CLC. [16] Moreover, energy compensation for gas separation is overcome since CO\textsubscript{2} is inherently separated in CLC. Another advantage of CLC is that the generation of NO\textsubscript{x} is avoided as no N\textsubscript{2} is presented in the fuel reactor.

**Fig.1 - Schematic representation of the CLC process.**

1.4. **Chemical looping with oxygen uncoupling**

To combust solid fuels, chemical looping with oxygen uncoupling (CLOU) represents an advantage compared to CLC. In CLOU process, oxygen carrier in the FR releases gaseous oxygen through decomposition according to reaction (3).

\[
\text{Me}_x\text{O}_y \leftrightarrow \text{O}_2 + 2\text{Me}_x\text{O}_{y-1} \quad (3)
\]

Thus, gas-phase oxygen reacts with the fuel according to reaction (4).

\[
\text{C} + \text{O}_2 \leftrightarrow \text{CO}_2 \quad (4)
\]

Since the contact between gas and solid molecules are more efficient than the solid-solid contact, CLOU is more favorable for solid fuel combustion than CLC. And by applying CLOU, slow gasification step can be escaped. [17][18] But from thermodynamic point of view, CLOU puts...
restrictions on oxygen carriers. Not all oxygen carriers have appropriate thermodynamics properties to release O\(_2\) in the FR. Some metal oxides systems, such as CuO/Cu\(_2\)O, Mn\(_2\)O\(_3\)/Mn\(_3\)O\(_4\) and Co\(_3\)O\(_4\)/CoO have been proved having suitable equilibrium oxygen partial pressures at temperature 800-1200ºC, thus having the ability to release gaseous oxygen in FR under combustion conditions. [19]

**Fig.2 – The equilibrium O\(_2\) partial pressure of Mn\(_2\)O\(_3\)/Mn\(_3\)O\(_4\) system as a function of temperature.**

Equilibrium oxygen partial pressure as a function of temperature for Mn\(_2\)O\(_3\)/Mn\(_3\)O\(_4\) system is presented in Fig.2. At lower temperature or higher oxygen partial pressure, Mn\(_2\)O\(_3\) is the stable phase. At higher temperature or lower oxygen partial pressure conditions, decomposition of Mn\(_2\)O\(_3\) to Mn\(_3\)O\(_4\) occurs with the release of gaseous oxygen. Assuming that AR has a temperature of 811ºC and the outlet concentration is 5%, Mn\(_2\)O\(_3\) is the phase presenting in solid stream. Whereas, in FR where O\(_2\) concentration is 0% (assuming a same temperature as in AR), Mn\(_3\)O\(_4\) is the stable phase suggested by Fig.2. So when the oxidized oxygen carrier is circulated from the AR to the FR, it releases gaseous O\(_2\) due to Mn\(_2\)O\(_3\) to Mn\(_3\)O\(_4\) phase transition. This released O\(_2\) can be directly used for fuel combustion. After reduction, oxygen carrier particles will be oxidized in the air reactor again.

1.5. Oxygen carriers

For CLC to be application feasible, some properties are demanded on oxygen carriers. These are: sufficient reaction rate of oxidation and reduction, ability to perform high conversion of fuel to CO\(_2\) and H\(_2\)O, good fluidizing properties, resistance against attrition and fragmentation, life time corresponding to the price and friendliness towards environment. [20] Many materials have
been studied, and the potential candidates are: Ni-based, Cu-based, Mn-based and Fe-based oxides. [21]

Fluidizing ability is a key factor that needs to be taken into consideration when an oxygen carrier is evaluated. It is deemed particles have good fluidization property if no agglomeration or channel formation is observed under experimental period. Numerous factors may affect fluidization property of particles, such as size and shape of particles, size distribution of solids, vessel geometry, gas inlet arrangement, type of solid, degree of moisture and so on. [22] Reichold et al. described that the tendency to defluidize increases with increased temperature, and becomes less likely with increasing gas velocity and mean particle diameter of the bed material. [23]

Some support materials, aiming to improve oxygen carriers’ resistant towards attrition, have been investigated (e.g. Al₂O₃, ZrO₂, TiO₂, SiO₂, MgO). In some cases, they may react with the active phase of an oxygen carrier forming new compounds which might affect the original properties of the oxygen carrier.

Another issue is carbon formation and its mechanism can be generally described by eq.(5)(Boudouard reaction) and eq.(6). Carbon formation has been noticed when operating some oxygen carriers. Metallic Ni is a catalyst for both eq.(5) and eq.(6). So if NiO oxygen carrier was further reduced and exposed to fuel rich condition, carbon formation can easily occur. Deposited carbon has been reported existing at the exit of FR reactor when operating some Mn-based particles. [24]

\[
\begin{align*}
2\text{CO} & \leftrightarrow \text{CO}_2 + \text{C} \quad (5) \\
\text{CH}_4 & \leftrightarrow \text{C} + \text{H}_2 \quad (6)
\end{align*}
\]

1.5.1. Mn oxides oxygen carriers

Manganese oxide is characterized by its low price, abundance in natural reserves and promising performances reported as a CLOU material, which makes it a potential applicable OC.

The oxidation and reduction behavior of manganese oxides has been studied by E.R. Stobbe et al.[25] It was found that both MnO₂ and Mn₃O₄ had the ability to convert CH₄ at temperature above 800°C. When re-oxidize the reduced sample by 5% O₂(compensated by Ar) at 800°C, Mn₃O₄ was the identified phase instead of Mn₂O₃, even though Mn₂O₃ was the thermodynamic stable phase.[25] The suggested reason in the literature for this contradictory result was that the oxidation condition (5% O₂ and 800°C or temperature above) was too close to the Mn₂O₃/Mn₃O₄ equilibrium condition. So the driving force for Mn₃O₄ oxidation to Mn₂O₃ was
too low. Thus, to oxidize Mn$_3$O$_4$ to Mn$_2$O$_3$, either higher oxygen partial pressure or lower operation temperature was recommended.

The problem that Mn$_3$O$_4$ cannot be oxidized by lower oxygen partial pressure at high temperature is a barrier for Mn$_2$O$_3$ being applied in CLC as oxygen carrier. Except decreasing oxidation temperature or increasing oxygen partial pressure, another option to avoid the Mn$_3$O$_4$ oxidation difficulty is to combine Mn with other element forming combined oxides. Forming combined oxides could be useful to alter the thermodynamic properties of manganese oxides, thus allowing the oxidation occurring under the described situation. Combined manganese iron oxides ((Mn$_{0.8}$Fe$_{0.2}$)$_x$O$_y$) was examined as oxygen carrier and presented promising results in a batch reactor system. These oxygen carriers showed CLOU property at 850°C with fast releasing rate, comparable to CuO-Cu$_2$O system, and complete conversion of CH$_4$. [26] Shulman et al. examined a combined manganese iron oxide with a composition of 80 wt%Mn$_3$O$_4$ and 20 wt%Fe$_2$O$_3$. The oxygen carrier’s reactivity was observed increasing with conducted CH$_4$ cycles in a 41 cycles test. [27]

Magnesium oxides with addition of calcium hydroxide have been mixed with manganese oxides as well. Some of these materials showed very high reactivity towards CH$_4$ and no carbon formation was detected. The addition of calcium hydroxide facilitates oxygen release and combustion of CH$_4$. [28]

Another idea to produce combined manganese oxygen carrier is mixing Si with Mn. By adding Si into manganese oxides, different manganese silicates are formed depending on the actual composition and synthesis temperature. Fig.3 is a phase diagram of Mn-Si-O system in air.[29] As can be seen in the figure, manganese silicates can transform to a lower Mn valence phase at higher temperature, together with releasing of oxygen. This means that Mn-Si-O materials have CLOU property theoretically. And examination of Mn-Si-O oxygen carriers is of great interest.
Fig. 3 – Phase diagram of Mn-Si-O system in air [29]

An overview of combined manganese oxides that have been studied for CLOU application can be found elsewhere in literature. [30]
1.6. **Objective**

The aim of this project is to evaluate synthetic manganese silicate oxygen carriers for CLC and CLOU. In this work, 5 oxygen carrier materials with different Mn/Si ratio were manufactured by spray-drying and examined with respect to CLOU behaviour and CH$_4$ conversion at temperature 900ºC-1100ºC in a batch fluidized bed reactor system.
2. Experimental

2.1. Experimental setup

Oxygen carrier’s reactivity test was performed in a batch fluidized bed system. As shown by Fig.4, the quartz reactor, which was 870 mm long and 22 mm in inner diameter, was enclosed in an electrical oven. In the quartz reactor, oxygen carrier was placed on a porous plate which was situated 370 mm from the bottom of the reactor. Temperature was measured 5 mm under and 10 mm above the porous plate by thermocouples enclosed in quartz shells. To examine fluidizing conditions, Honeywell pressure transducers with a frequency of 20 Hz were used to measure pressure drop over the bed.

Gas mixture of pure gas was introduced from the bottom of the reactor, reacted with oxygen carrier and left the reactor from the top. Outlet gas was first cooled by an electric cooler where the steam was condensed. Then the dry gas stream was sent to a gas analyser (Rosemount NGA-2000) where the volume fractions of CO, CH₄, CO₂ and O₂ together with a total volumetric flow were determined. Flue gases were driven to ventilation eventually.
2.2. Manganese silicate particles in this study

Oxygen carriers investigated in this work were manufactured by spray drying. Detail information about spray-drying process was presented elsewhere in literature. [31] After spray-drying, produced particles were calcined at 1050ºC for 4 hours. Particles with diameter 125-180µm were sieved for reactivity test. In this project, the amount of Mn$_2$O$_3$ in raw material varied from 98 wt% to 50 wt%. A summary of raw material composition for spray-drying can be found in Table 1.

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>wt%Mn$_2$O$_3$</th>
<th>wt%SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>M2</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>M3</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>M4</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>M5</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

2.3. Reactivity test of manganese silicate oxygen carrier

Evaluation of manganese silicate particles was divided into 3 parts:

- **Part 1:** Examine materials’ CLOU property, reactivity towards syngas (50% CO and 50% H$_2$) and CH$_4$ at temperature 900ºC to 1100ºC after oxidation by 5% O$_2$.
- **Aim 2:** Examine oxygen carriers’ CLOU behaviour under oxidation of 21%O$_2$.
- **Aim 3:** Examine stability of oxygen carrier’s CLOU behaviour at a specific temperature by conducting multiple cycles after oxidation in 21%O$_2$.

In part 1, 15 grams of oxygen carrier was placed on the porous plate in the quartz reactor and heated to 900ºC under 5%O$_2$ (compensated by N$_2$). To activate oxygen carrier material, a syngas flow (450 mL/min) was injected into the reactor for 80s. After syngas reduction, particles were alternatively exposed to oxidation (5% O$_2$) and reduction (by CH$_4$ for 20s) environments, thus simulating the cyclic conditions of a CLC unit. A N$_2$ stream was injected for 60s before and after fuel inlet to avoid back-mixing of O$_2$ and fuel. In CH$_4$ cycles, CO$_2$ fraction was obtained, which can be directly related to CH$_4$ conversion, i.e. oxygen carrier’s reactivity towards CH$_4$. Following two CH$_4$ cycles, two inert cycles were carried out, where N$_2$ (600 mL/min) was used to flush the reactor for 360s after particles being fully oxidized. This was to measure materials’ CLOU property i.e. how much O$_2$ particles can release. Operation temperature was increased to next level during oxidation step after the two inert cycles were
finished. At each temperature, two CH₄ cycles and two inert cycles were performed as described above. Experimental temperature was set to 900°C, 1000°C, 1050°C and 1100°C.

Two oxygen carriers (M3 and M5), which presented better properties in part 1 test, were selected for part 2 test. Similar as performed in part 1, one syngas cycle and two inert cycles were conducted at each temperature, i.e. 900°C, 950°C, 1000 °C, 1050°C and 1100°C, after particles were fully oxidized. Since M5 material showed better results, it was tested in an additional temperature range: 925°C, 975°C, 1025°C and 1075°C. In part 2, the oxidation condition was air which was different from part 1.

The stability of M5 oxygen carrier regarding CLOU property was evaluated in test Part 3. Experimental temperature was set to 1000°C, where M5 material demonstrated highest reactivity observed from the first part of the work. In this part of test, M5 particles were firstly activated by conducting four syngas cycles (80s syngas injection in each cycle). Then, eight inert cycles (N₂, 360s flushing) were performed. After both syngas and N₂ cycles, air was used to oxidize the sample.

Fresh particles were used in all three parts of tests. Gas composition and flows were summarized in the table below.

*Table 2. Summary of the gas flows in each cycle. *(f)Only one fuel is used in each cycle.*

<table>
<thead>
<tr>
<th>AIM 1</th>
<th>Cycle</th>
<th>Oxidation</th>
<th>Inert</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air (21% O₂, 79% N₂)</td>
<td>216,35 ml/min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>683,65 ml/min</td>
<td>600 ml/min</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CH₄*(f)</td>
<td>-</td>
<td>-</td>
<td>450 ml/min</td>
<td></td>
</tr>
<tr>
<td>Syngas (50% H₂, 50% CO) *(f)</td>
<td>-</td>
<td>-</td>
<td>450 ml/min</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AIM 2&amp;3</th>
<th>Cycle</th>
<th>Oxidation</th>
<th>Inert</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air (21% O₂, 79% N₂)</td>
<td>600,55 ml/min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-</td>
<td>600 ml/min</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Syngas (50% H₂, 50% CO)</td>
<td>-</td>
<td>-</td>
<td>450 ml/min</td>
<td></td>
</tr>
</tbody>
</table>

Crystalline phases of M5 particles were identified by X-ray powder diffraction. Fresh samples, samples oxidized by 5% O₂ air and syngas reduced sample were examined. The oxidized samples were obtained by exposing the fresh sample to an oxidizing flow (5%O₂ or 21%O₂, respectively) at 1000°C for 45 minutes, and then cooled in the respective oxidizing flow as rapid as possible to room temperature. The reduced sample was achieved by running syngas through the reactor at 1000°C for 15 minutes, ensuring the reduction of the whole sample, and cooled down to room temperature in syngas.
2.4. Data Analysis

Gas yield ($\gamma$) is used to gauge the reactivity of an oxygen carrier towards a fuel. It is defined as the percentage of a product compound over the total amount of compounds in the outlet stream. In this study, gas yield is chosen as the CO$_2$ percentage in the outlet stream. With CH$_4$ or syngas as reducing gas, $\gamma$ is expressed as follows:

$$\gamma = \frac{x_i}{\sum_{i=1}^{n} x_i} \quad (7)$$

where $x_i$ is the fraction of component $i$ (for CH$_4$ cycle $i=$CO, CO$_2$ and CH$_4$; for syngas cycle, $i=$CO and CO$_2$) in the dry outlet gas. CO$_2$ is used to calculate gamma as it is the most oxidized product. The gamma value ranges from 0 to 1, where 1 refers to complete conversion.

The degree of mass-based conversion, $\omega$, is defined as the mass of the oxygen carrier divided by the mass when it is fully oxidized:

$$\omega = \frac{m}{m_{ox}} \quad (8)$$

Since $m$ is not practical to be directly measured, it can be calculated as a time integral during a reduction period. When CH$_4$ was used as fuel, it can be obtained by equation 9:

$$\omega_i = \omega_{i-1} - \int_{t_0}^{t_1} \frac{n \dot{M}_0}{m_{ox}} (4x_{CO_2} + 3x_{CO} - x_{H_2}) dt \quad (9)$$

where $n$ is the molar flux of the dry outlet stream and $M_0$ is the molar mass of oxygen. When syngas is the fuel, $\omega$ can be calculated as:

$$\omega_i = \omega_{i-1} - \int_{t_0}^{t_1} \frac{n \dot{M}_0}{m_{ox}} (2x_{CO_2} + x_{CO} - x_{H_2}) dt \quad (10)$$
3. Results and discussion

3.1. Reactivity towards syngas

At the beginning of test part 1, one syngas cycle was performed at 900°C after sample particles were fully oxidized. This syngas cycle aimed to activate oxygen carrier particles and the gas conversion in the cycle was analyzed to present material’s reactivity towards syngas.

![Fig.5 – Dry gas concentration profile of outlet stream in a syngas cycle performed on M3 sample.](image)

Fig.5 is an example of dry gas concentration profile of a syngas cycle at 900°C, where M3 material was chosen. At t=0 s, 5% O\textsubscript{2} was switched off and pure N\textsubscript{2} was inlet into the system for 60 s. The decreasing of O\textsubscript{2} concentration cannot be noticed until t= 20 s due to a delay of the measuring system. At t=80 s, syngas was injected into the reactor while N\textsubscript{2} was turned off. At this time, a rapid raising CO\textsubscript{2} concentration was detected suggesting that the inlet syngas was fast converted into CO\textsubscript{2} by M3 oxygen carrier. Reading from the figure, one can see that O\textsubscript{2} concentration increased considerably from 5% (oxidizing condition) till over 20% after syngas injection. Syngas conversion over manganese silicate oxides was highly possible an exothermal reaction suggested by measured increasing temperature. This could be a cause for the increased O\textsubscript{2} concentration. Referring to Fig.3, as surrounding temperature increased, the manganese silicate can decompose to a lower Mn valence manganese silicate, which released more O\textsubscript{2} compared with the case having a stable temperature. During calcination, oxygen carrier particles were heated and cooled down to room temperature in air. Under such a circumstance, some O\textsubscript{2} may be trapped in the particles due to solid shrinkage. These O\textsubscript{2} might be released during syngas reduction cycle as a result of particle expansion. Thus, these trapped O\textsubscript{2} could be the main reason for the observed huge amount of released O\textsubscript{2} as manganese silicate phase transition.
is theoretically not able to provide such a quantity of O\textsubscript{2}. Afterwards when oxygen concentration decreased till 0%, just CO\textsubscript{2} was detected. Gas yield of syngas was calculated and full conversion was obtained. For the other tested oxygen carriers, the O\textsubscript{2} concentration peak during syngas reduction cycle varied from 7% to 24%. But all materials achieved full conversion of syngas. Therefore, oxygen carriers’ reactivity towards fuel was focused on CH\textsubscript{4} conversion.

Fig.6 – Gas yield (γ) as a function of mass-based conversion (ω) for M3 carrier using syngas as fuel

3.2. Reactivity towards CH\textsubscript{4}

CH\textsubscript{4} is the primary constituent of natural gas which may be an alternative fuel instead of coal in the future.

In part 1 test, two CH\textsubscript{4} cycles were executed at each temperature (900ºC, 1000ºC, 1050ºC and 1100ºC). Some information at high temperatures is missing due to de-fluidization problem of some samples. The dry gas concentration profile of the 2nd CH\textsubscript{4} cycle performed on sample M3 at 1000ºC is presented in Fig.7 for demonstration. At 30s<\textless t<90s, all carbon gas concentrations were 0 since the reactor was purged by a nitrogen stream. During the fuel cycle (80s<\textless t<100s), 93% of CH\textsubscript{4} was converted to CO\textsubscript{2}, despite of a small amount of unreacted CH\textsubscript{4}. 
Fig. 7 – Dry gas concentration profile of outlet stream for the 2nd CH$_4$ cycle at 1000ºC performed on M3 sample.

Fig. 8a shows the CH$_4$ yield ($\gamma$) as a function of the solid conversion ($\omega$) for M3 carrier investigated at four different temperatures. Black colored lines present results obtained from the first CH$_4$ cycle and red colored lines are the situations for the second CH$_4$ cycle. As seen in the figure, M3 sample’s reactivity was almost identical for the two CH$_4$ cycles performed at the same temperature. Generally, the gas conversion was high at higher experimental temperatures. In some cases (M1 or M2), particles performed forming channels or soft agglomerations at temperatures over 1050ºC, resulting in fluidization problems.

Fig. 8a – Gas yield ($\gamma$) as a function of mass-based conversion ($\omega$) for M3 carrier using CH$_4$ as fuel.
The $\gamma$-\(\omega\) plots for M4 particles at different temperatures are presented in Fig. 8b. Compared with M3 sample, see Fig. 8a, M4 particles presented a different behavior. The reactivity of M4 materials increased with experimental temperature from 900°C till 1000°C. Further temperature increase resulted notably deactivation shown by the dotted lines and dashed lines in the figure below. Severe deactivation of material’s reactivity towards CH\(_4\) at higher temperature was only observed on M4 sample.

![Sample M4: 50% Mn\(_2\)O\(_3\), 50% SiO\(_2\)](image)

**Fig. 8b – CO\(_2\) yield ($\gamma$) as a function of mass-based conversion ($\omega$) for M4 carrier using CH\(_4\) as fuel.**

Fig. 9 summarizes the CH\(_4\) conversion at four experimental temperatures for all tested manganese silicate oxygen carriers. Each point refers to an average CH\(_4\) conversion at a certain temperature from where a comparison among the examined samples can be accomplished. At 900°C, gas yield ranged from 70 to 80% for all the particles, except for M1. Although M1 possessed the highest composition of manganese oxide, it presented the lowest reactivity towards the fuel at temperature range 900°C to 1000°C. It seems that samples with higher Si content had better reactivity at temperature 900°C to 1000°C. In this temperature range, manganese silicate oxygen carriers’ reactivity increased obviously with experimental temperature. Sample M2, M3 and M5 retained full CH\(_4\) conversion under high temperature conditions, i.e. 1050°C and 1100°C. On the other hand, M1 sample suffered defluidization at 1100°C and M4 material’s reactivity sharply decreased when temperature increased from 1000°C to 1100°C.

Compared with pure manganese oxides, addition of Si indeed improved oxygen carriers’ properties. [21] During experimental process, no difficulty in oxidizing Mn-Si oxygen carrier at
temperature above 900ºC was observed. Material M2, M3 and M5 even had the ability to fully convert CH₄ at 1100ºC without any defluidization problem, which is very promising. The amount of added SiO₂ needs to be appropriate. Sample M1 with 2 wt% SiO₂ in recipe encountered defluidization problem at higher temperature, and M4 particles with 50 wt% SiO₂ in raw materials had extremely low reactivity at higher temperature. Suggested amount of SiO₂ to combine with Mn₃O₄ is between 6 wt% to 30 wt%.

The different behavior of M4 material, i.e. low reactivity at higher temperature, compared with the other tested materials may be briefly explained as follows. Referring to Fig.3, M4 sample containing 50 wt% of SiO₂ lay on the right hand side of the Mn-Si-O phase diagram, while the rest of tested samples lay at the left hand side of the phase diagram. At higher temperature, M4 sample fall into MnO•SiO₂ solid solution area and MnO is the most reduced phase of Mn oxides. This might be the reason for the extremely low reactivity of M4 sample at temperature above 1050 ºC. For M1, M2, M3 and M5 samples, several other manganese oxide phases with lower Mn valences exit at higher temperature, which could facilitate further reduction of oxygen carriers. This might explain the behavior that these samples maintained high reactivity at higher temperature.

Fig.9 – Summary of CH₄ conversion at tested temperatures for five examined manganese silicate oxygen carriers.
3.3. CLOU property after oxidation by 5% O₂

Oxygen carriers’ CLOU property was evaluated by operating inert cycles and measuring the O₂ concentration in the outlet stream. Since CLOU process is more favorable than CLC process, CLOU property of an oxygen carrier is an important factor to evaluate.

In test part 1, two inert cycles were conducted at temperature 900ºC, 1000ºC, 1050ºC and 1100ºC after CH₄ cycles. The O₂ concentration as a function of time for the second inert cycle at 1000ºC is plotted in Fig.10. At t=0 s, 5% O₂ used for particle oxidation was switched off and pure N₂ was sent into the system for 360 s. The O₂ concentration did not drop down until t=20 s. This was due to a system delay as described before. The O₂ concentration did not go to 0 immediately, but maintained at a certain level which was resulted from materials CLOU property.

Taking a closer look at the last 60 s of the O₂ concentration profile, presented in Fig.11, one can find that these manganese silicate oxygen carriers did not release too much O₂ at 1000ºC. And material M4 and M5 which had higher SiO₂ contents released more O₂ than the other materials at 1000ºC.
Fig.11 – The last 60 s of the O\textsubscript{2} concentration profile of the 2nd inert cycle at 1000ºC for all tested materials.

Fig.12 summarizes the concentration of released O\textsubscript{2} for all tested materials at four experimental temperatures. At each cycle, the O\textsubscript{2} concentration at t=360 s was selected to present material’s CLOU property. The average value of two cycles at the same temperature was calculated to gauge material’s CLOU property at this temperature. These calculated average value were plotted as a function as temperature and shown in Fig.12.

As shown in the following figure, manganese silicate oxygen carriers’ CLOU property was suppressed at low temperature. With temperature increase, from 900ºC to 1000ºC, CLOU property of all tested materials was promoted. At 1050ºC, M1 material first encountered defluidization problem. Later, sample M2 and M5 had difficulty in fluidization at 1100ºC. Though M4 material did not have fluidization difficulty, its CLOU property greatly diminished when the experimental temperature increased above 1000ºC. On the other hand, the CLOU property of M3 particles which had 30 wt% Si content improved with increasing temperature. The released O\textsubscript{2} by M3 particles increased from 0.1% at 900ºC and reached a maximum of 0.7% at 1100ºC.
3.4. CLOU property after oxidation by air

Based on the results in section 3.3, two oxygen carriers M3 and M5, which presented better results at high temperatures, were chosen to investigate in part 2 test. In this part of test, particles were oxidized by air, i.e. 21% O$_2$, instead of 5% O$_2$. And experimental temperatures were set to 925°C, 975°C, 1025°C and 1075°C. Detailed experimental procedure can be found in section 2.3.

In Fig.13, the O$_2$ concentration profile of inert cycles for M5 sample is presented. Oxygen carrier particles were fully oxidized by synthetic air before exposed to pure N$_2$ for 360s. The
A drop of O$_2$ concentration was not observed until $t= 20$ s, though the N$_2$ flow was switched on at $t=0$ s. The O$_2$ concentration of the last 60 s is shown in Fig.14, where the influence of temperature is clearly seen. Generally, the M5 material’s CLOU property improved with temperature. The maximum released O$_2$ was achieved at the highest experimental temperature 1075°C, and almost no O$_2$ was released at 925°C. At 1025°C, M5 material’s CLOU property was surprisingly low. Unfortunately, the reason for this is yet unknown and thus needs to be investigated in the future.

![Fig.14](image1.png)

**Fig.14** – The last 60 s of the O$_2$ concentration profile of the 2nd inert cycle for M5 materials.

![Fig.15](image2.png)

**Fig.15** - The average released O$_2$ concentration for M3 and M5 carriers after oxidation by air.
Fig. 15 summarizes the released oxygen concentrations at tested experimental temperatures of M3 and M5 particles after oxidation under air conditions. As described in section 3.3, the average value was calculated from O₂ concentration at t=360 s of which two inert cycles were performed at the temperature. From the figure, M3 material’s CLOU property clearly showed an increasing trend with experimental temperature. At temperature range 1000°C to 1050°C, M3 materials’ CLOU property was greatly promoted. While, the relationship between experimental temperature and CLOU property for sample M5 was not very straightforward. Positive effect of increasing temperature on material’s CLOU property was observed from 900°C to 1000°C. Then CLOU property was sharply suppressed at 1025°C. With further increasing of experimental temperature, M5 material’s CLOU property was improved. The variability of trends may indicate more than one phase change occurred in temperature range 900°C and 1100°C for M5 particles.

![Graph showing oxygen concentration vs temperature for M3 and M5 materials](image)

Fig. 16 – Average released O₂ concentration for M3 and M5 carriers after oxidation by 5% and air

Fig.16 compares the average CLOU O₂ concentration in inert cycles after air and 5% O₂ oxidation for M3 and M5 particles. Red colored lines present the results obtained from air oxidation condition and black lines showed the 5% O₂ oxidation condition. Oxidation by a higher O₂ partial pressure stream apparently benefited materials’ CLOU property. The positive effect of higher O₂ partial pressure was extremely important at higher temperature. Both M3 and M5 material released more than double amount of O₂ after oxidation by air than by 5% O₂ comparing the red dots and black ones at temperature 1050°C and above. This effect is theoretically logical since equilibrium O₂ partial pressure for a certain phase transition is higher at higher temperatures. So, higher O₂ partial pressure is required to be able to oxidize oxygen carrier particles in some cases. With higher O₂ partial pressure, the particles may be more oxidized as the driving force is bigger compared with oxidation by a lower O₂ partial pressure stream.
3.5. CLOU behavior in multiple cycles

The stability of a material’s CLOU behavior is a key factor in CLOU. Oxygen carrier M5 was selected for the stability test which was described in part 3 test in section 2.3. At 1000°C, a syngas cycle and an inert cycle were run alternatively for four times. Afterwards, eight inert cycles were executed.

![Graph showing oxygen concentration released by M5 carrier at 1000°C in multiple inert cycles.](image)

**Fig.17 – Oxygen concentration released by M5 carrier at 1000°C in multiple inert cycles.**

Fig.17 presents the oxygen concentrations released by M5 carrier at the end of inert cycle where t=360 s. Particles were previously oxidized by 21% O<sub>2</sub> air. As seen from the figure, the CLOU property of M5 decreased obviously along the number of performed cycles. Time of oxidation, which was indicated below each experimental point, seems to be a factor influencing how much oxygen can be released in the following inert cycle. However, the deterioration of CLOU ability cannot be fully overcome by increasing oxidation time as implied by the last three cycles. Since experimental condition was thermodynamically sufficient to fully oxidize the particles, the decreasing of CLOU property with prolonged cycles may be caused by a low diffusion inside the particles.
3.6. M5 phase analysis by XRD

Table 3 presents the XRD identified crystalline phases on M5 samples. Fresh sample was the particles before running any gas cycles. Oxidizing samples were the ones oxidized by the indicating gases at 1000°C for 45 minutes, and then cooled in 5%O₂ or synthetic air, rapidly to room temperature. Reduced samples were obtained by reducing the sample by syngas for 15 min and fast cooled to room temperature in syngas flow.

Surprisingly, particles oxidized by 5% O₂ and reduced by syngas, column 2 and 3, had the same composition. This was theoretically impossible as the material converted syngas losing oxygen and being reduced. Since XRD scanning period was set to 15 min which was quite short at some point, there could be some information missing or hiding in the low intensity area in the result diffraction spectra. This is a factor needs to be taken into consideration.

Particles oxidized by air and then reduced by syngas presented a different phase compared with air oxidized sample, see column 4 and 5 in Table 3. In the reduced sample, tephroite Mn₂SiO₄ was identified instead of rhodonite MnSiO₃ in the oxidized sample. At 1000°C, reaction between braunite and rhodonite forming tephroite seems to be the reaction contributing to syngas conversion for particles oxidized by air. This mechanism, where the different phases were actually detected in this work, was also suggested by Rydén et.al. [30]

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>M5 (70 wt% Mn₃O₄, 30 wt% SiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1000°C</td>
</tr>
<tr>
<td>Oxidizing/Reduction gas</td>
<td>(Fresh sample)</td>
</tr>
<tr>
<td>Phases identified</td>
<td>Braunite-1Q (Mn₇O₈(SiO₄))</td>
</tr>
<tr>
<td>Rhodonite (MnSiO₃)</td>
<td>Rhodonite (MnSiO₃)</td>
</tr>
</tbody>
</table>

In the case of M4 particles, a remarkable physical change took place. The bed material turned its color from initial brown to ash grey after test part 1. Seemingly, it may be caused by irreversible formation of silicate.
4. Conclusions

Five combined manganese silica samples with different Mn:Si ratio have been investigated in this work. The percentage of silica in raw materials increases from 2wt%, 6wt%, 10wt%, 30wt% to 50wt%. The following conclusions can be drawn:

- All manganese silicate oxygen carriers presented high reactivity towards syngas at 900°C.

- Particles with a composition of silica between 6wt% and 30wt% showed great reactivity towards CH\textsubscript{4} at temperature 900°C to 1000°C. Furthermore, SiO\textsubscript{2} seems to improve materials’ fluidization properties.

- Seemingly, materials CLOU property increased with silica content. Materials M4 containing 50 wt% SiO\textsubscript{2} and M5 with 30 wt% SiO\textsubscript{2} demonstrated better CLOU properties among the tested materials between 900°C and 1050°C. But at higher temperature 1100°C, M3 material consisting of 10 wt% SiO\textsubscript{2} and 90 wt% Mn\textsubscript{3}O\textsubscript{4} released about 0.7% O\textsubscript{2} which performed best.

- M3 material presented an increasing trend of releasing oxygen with increased temperature under experimental conditions.

- M5 proved to release the highest percentage of gaseous oxygen (1.4% O\textsubscript{2}) at 1100°C in N\textsubscript{2}.

- The CLOU property of sample M5 decreased apparently when multiple inert cycles are carried out.
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