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## Evaluation of ilmenite, manganese ore, LD slag and iron sand oxygen carriers for chemical looping gasification with microalgae

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#### ARTICLE INFO ABSTRACT Keywords: Microalgae could be a sustainable feedstock for production of liquid biofuels. However, as such fuels contain Chemical looping gasification significant fractions of reactive ash species, it is necessary to deploy synthesis routes which can handle such Oxygen carrier "dirty" fuels. Chemical-looping gasification (CLG) has the potential to convert such feedstocks and generate a Microalgae concentrated syngas stream, a common precursor for liquid fuel production. Suitable functional oxygen carriers Catalysis are key for CLG, and herein we report our new work in fluidized-bed tests with four oxygen carriers, namely ilmenite, MnGBhne, LD slag and iron sand. These materials are economically viable natural ores or industrial byproducts. The oxygen carrier is reduced to different oxidation degrees (0.2, 0.5, 1) at typical temperatures (850, 900, 950 °C) to define equal material states prior to the gasification. We found that the LD slag and iron sand had the highest gasification rate and fluidized well without agglomeration, thus they are selected as suitable oxygen carriers for the process. Several factors including catalysis, water splitting and water-gas shift are comprehensively discussed with regard to the outstanding performance of LD slag and iron sand. Calcium catalysis is

deemed as a key reason for the fast gasification and a mechanism of this is proposed.

#### 1. Introduction

Carbon capture and storage (CCS) is seen by many actors as important route for meeting climate targets [1]. Biomass gasification integrated with CCS generates bioenergy with carbon capture and storage (BECCS) while attaining negative carbon emissions [2]. Chemical looping gasification (CLG) is a novel BECCS technology, where the air and fuel are not mixed, and thus it generates a concentrated and undiluted syngas stream [3]. Therefore, this process doesn't need intensive nitrogen separation that is usually required in conventional gasification [4]. The syngas produced is an important building block for many synthesis processes, e.g., Fischer–Tropsch process, and can also be converted to green  $H_2$  [5].

CLG is developed based on and takes advantages of chemical looping combustion technology [6,7]. Fig. 1 presents a schematic description of the CLG technology. CLG has an air reactor and a fuel reactor and a medium called oxygen carrier. The oxygen carrier circulates between the two reactors for oxygen and heat transfer from the air reactor (exothermic reactions) to the fuel reactor (endothermic gasification). The oxygen carrier is usually oxides of transition metals (Me<sub>x</sub>O<sub>y</sub>) that are reduced (to Me<sub>x</sub>O<sub>v-1</sub>) by fuel in the fuel reactor to provide oxygen and heat for gasification and are then re-oxidized by air in the air reactor. General reactions in the two reactors are presented in reaction r1-r6below. In the fuel reactor, the fuel is rapidly heated and devolatilized through reaction *r1* generating volatiles and char at high temperatures. The char is then gasified with  $H_2O$  and/or  $CO_2$  via reaction r2 and r3. A part of the gasification products (H2 and CO) and volatiles (CHm/H2/ CO) could be converted with the oxygen carrier (reaction r4) to generate CO2 and heat that can compensate heat for the gasification reaction. Because air is not present in the fuel reactor, the fuel-reactor gas stream is not diluted. If the CO<sub>2</sub> is captured, the process becomes negative carbon emissions, in addition to biofuels production. The reduced oxygen carrier is then transferred to the air reactor and regenerated with air through reaction r5. In some undesired cases, part of the char may mix with the oxygen carrier and then be transferred to the air reactor and burnt with air. This generates  $CO_2$  (reaction r6) that may be emitted with the depleted air. But this type of carbon emission can be well avoided by implementing, e.g., a carbon stripper between the fuel and

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Fig. 1. Principle of Chemical Looping Gasification technology.

air reactor [8].

 $Fuel \rightarrow Volatiles(g) + Char(C + ash)$ (r1)

 $Char(C + ash) + H_2O \rightarrow H_2 + CO + ash$ (r2)

 $Char(C + ash) + CO_2 \rightarrow 2CO + ash$  (r3)

Volatiles/CH<sub>m</sub>/H<sub>2</sub>/CO + n Me<sub>x</sub>O<sub>y</sub> $\rightarrow$ H<sub>2</sub>O + CO<sub>2</sub> + n Me<sub>x</sub>O<sub>y-1</sub> (r4)

 $Me_xO_{y-1} + Air \rightarrow Me_xO_y + depleted Air$  (r5)

 $Char(C + ash) + O_2 \rightarrow CO_2 + ash$  (r6)

Regular biomasses have been extensively studied in CLG process, and the syngas generated can be used for biofuels production. These biomasses are based on either food or non-food crops and woods, so the biofuels are either 1st-generation (food) or 2nd-generation (non-food) [9]. Microalgae are special biomass and have low costs, large availability [10] and fastest growing rate [11]. What is more, they can be found in wide water areas (fresh, waste waters and marine systems) [12,13]. In addition, microalgae have no effect on the food chain and have high capability of CO<sub>2</sub> assimilation [14], therefore, the liquid-fuels derived from microalgae are called 3rd-generation (3G) biofuels. CLG with microalgae has many advantages over conventional gasification processes, and this makes microalgae-CLG more economically viable and very competitive in getting higher revenues. However, few studies have used microalgae as feedstock in CLG process [15-18]. Even so, these few studies were conducted with microreactors working in a fixedbed form [15,16] without presence of steam and CO<sub>2</sub> gasifying agents [17,18] which are, however, important conditions for CLG process. These studies brought up impressive results encouraging more research on the microalgae-CLG process. One challenge with microalgae may lie in that they have significant content of ash, which is a "dirty" component and can lead to serious corrosions on heat-exchanger. CLG technology can address this issue because the fuel and heat-exchanger are in different reactor vessels [19]. However, the high ash content means that "oxygen carrier-ash" interactions likely happen [20], and this may limit the lifetime of oxygen carrier. So, it is essential to utilize materials which are economically viable and available in large quantities on the earth, for instance the Mn- and Fe based materials.

Ilmenite, manganese ore, LD slag and iron sand are all available globally at large volumes, established logistic chains and have been used in OCAC (a technology uses oxygen carriers) at larger scales [21-24]. Therefore, the four oxygen carriers are considered promising for use in microalgae-CLG process. Ilmenite which is a titanium-iron based natural ore has shown a high reactivity and a reasonable long lifetime [25,26], and is thus considered as a bench-mark oxygen carrier for scale-up of chemical looping technology [19,27,28]. Manganese ore is another natural ore of highly interest for chemical looping [29-34], because it has iron and manganese as the main components and is more reactive than ilmenite [31,32]. The MnGBhne is a recommended manganese ore in our previous work [30,31] and has been recently tested in a pilot for BCLG process [35], showing promising results for syngas yields in autothermic conditions. Alternative to natural ores, industry byproducts are receiving increasing interests for use as oxygen carrier in chemical looping process [36–39]. A steel converter slag called LD slag has been tested for CLG in a 1.5 kWth unit, and a high-quality syngas was obtained with low tar generation under autothermal conditions [40]. Another by-product called iron sand also emerged as an interesting oxygen carrier for CLG process [37]. Some of the four oxygen carriers have been subject to proof-of-concept with 1.5-25 kW<sub>th</sub> pilot reactors [41,42].

To our best knowledge, no operational experience with microalgae in CLG units is available, and suitable oxygen carriers need to be selected for this. Based on previous operational experience with other fuels, the oxygen transfer relies little on oxygen carrier's reactivity. Instead, the oxygen carried from air-reactor determines the rate of oxygen transfer which can be eventually adjusted with the air flow [28]. In this case the syngas yield and the fuel-reactor gas composition rely mainly on the oxygen transfer. But in some other cases, use of different oxygen carriers can also lead to different char conversion and syngas yield, even with a same oxygen transfer rate [23,28]. Therefore, the effect of oxygen carrier itself on the char gasification and the overall CLG performance should be identified during oxygen carrier screening process.

The aim of this work is to find suitable oxygen carrier for the microalgae-CLG process. Process performance in microalgae-CLG is studied with ilmenite, MnGBhne manganese ore, LD slag and iron sand oxygen carriers in typical reacting conditions. For faster oxygen carrier selection, a new evaluation methodology is developed and presented. In this methodology, oxygen carrier's reduction extents (oxidation degrees) were carefully adjusted to closer to real CLG conditions. In this case, conducting a small matrix of experiment can ensure us to get sufficient information for oxygen carrier selection. A batch fluidized bed reactor platform is employed to offer different reacting conditions. Key parameters analyses together with various characterizations are performed to elucidate the process and to select promising oxygen carrier.

#### 2. Experimental

#### 2.1. Oxygen carriers and microalgae

Ilmenite, MnGBhne, LD slag and iron sand are the oxygen carriers used in the work. The ilmenite and MnGBhne are a titanium-iron natural ore and a manganese-iron ore with their origin of Norway and Gabon, respectively. The LD slag and iron sand are industrial by-products from LKAB's Linz-Donawitz process and Boliden AB's copper plant, and they both were provided through Chalmers University of Technology. The ilmenite was from a previous campaign with biomasses in the 20 kW<sub>th</sub> unit at the group [43,44], and thus it is well heat treated before use in the current work. On the contrary, the MnGBhne, LD slag and iron sand are in fresh state, meaning no previous use in chemical looping process, so they were pre-treated before use. The LD slag and iron sand were calcined at 950 °C for 6 h to strengthen the particles and to lower the risk of agglomeration in fluidized beds [45,46]. The MnGBhne particles were calcined at 800 °C for 2 h to strengthen the particles and to take the advantages of gas-phase oxygen release from manganese oxides [47].

These different heat-treatment conditions were selected to get suitable particle properties for chemical looping process based on our experience. All the oxygen carrier particles were sieved to 100–300  $\mu$ m before use. Table 1 presents the composition of these oxygen carriers and their oxygen transport capacity (R<sub>OC</sub>) which is a key parameter in chemical looping process and calculated by dividing the maximum available oxygen mass over the corresponding oxygen carrier mass. The redox system and their calculated R<sub>OC</sub> are shown in Table 1. In addition, a zirconium dioxide (ZrO<sub>2</sub>) is used either as inert bed material for blank tests or as inert to dilute the oxygen carriers, as described below in Section 2.3. Its inert property has been confirmed with 5 % H<sub>2</sub> in a TGA test as described in the Supporting Information. The ZrO<sub>2</sub> particles have a high bulk density (around 4600 kg/m<sup>3</sup>) and thus we used a smaller size (100–200  $\mu$ m) than the oxygen carriers (bulk density range: 1300–3700 kg/m<sup>3</sup>) to avoid density-induced segregation during fluidization.

The Spirulina microalga is sourced from Brazil and was received in powder of several micron-meters. Before use, it was granulated with a granulator (Eirich EL1) by using deionized water as the only binder. Moisturized granulates were obtained from the granulation and then dried naturally at room temperature to get granulates with diameters below 3 mm. The dried granulates were then simply sieved to particles in-between 200 and 400 µm for use in the study. A proximate and ultimate analysis of the microalgal particles is displayed in Table 2 and this confirms the high volatiles and low fixed carbon content in the fuel, while the nitrogen (N) and ash content is higher than the average in biomasses [49]. The ash was obtained after air oxidation at 550 °C following a Spanish standard (UNE-EN ISO 18122:2023) [48] and has a high content of potassium (K), sodium (Na) and phosphorous (P) which can enhance the char gasification as well as incur ash-oxygen carrier interactions in chemical looping process [20]. Fig. 2 below shows that these ash components tend to form salts of sulphate, phosphate and chloride, and the main XRD phases are  $Na_{1.86}Al_{0.38}PO_4$ ,  $Na_{0.1}K_{0.9}Cl$  and some K<sub>2</sub>SO<sub>4</sub> and KCl. These compounds can be vaporized or decomposed easily at temperatures in chemical looping process and the generated alkalis can enhance the gasification process as well as interact with the bed materials.

#### 2.2. Batch fluidized bed reactor

The experiments were carried out in a fluidized bed reactor with bed material filled in "batch" fashion, see Fig. 3. This means a certain amount of the material is put into the reactor before the tests, while there are no "make-up" particles added or solids circulation during the experiments. The batch reactor has a gas preparation system which is composed by gas cylinders, mass flow controllers (MFCs), gas tubes and valves. With this gas system, various gas flows and concentrations can be prepared for different purposes. The gas stream can be mixed with steam which is generated by heating-up deionized water at a certain flow rate.

#### Table 1

| Property of the four | oxygen car | riers and | ZrO <sub>2</sub> . |
|----------------------|------------|-----------|--------------------|
|----------------------|------------|-----------|--------------------|

|                  | Particle size<br>dp (μm) | R <sub>oc</sub> <sup>a</sup><br>(-) | Major XRD phase<br>before tests                                     | Main active red-ox<br>system                                    |
|------------------|--------------------------|-------------------------------------|---|---|
| Ilmenite         | 100-300                  | 0.037                               | Fe <sub>2</sub> TiO <sub>5</sub> , Fe <sub>2</sub> O <sub>3</sub> , | Fe <sub>2</sub> TiO <sub>5</sub> /FeTiO <sub>3</sub> -          |
|                  |                          |                                     | TiO <sub>2</sub>  | Fe <sub>2</sub> O <sub>3</sub> /Fe <sub>3</sub> O <sub>4</sub>  |
| MnGBhne          | 100-300                  | 0.05                                | Mn <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> ,   | Mn <sub>3</sub> O <sub>4</sub> /MnO -                           |
|                  |                          |                                     | FeMnO3 <sup>d</sup> , SiO2  | Fe2O3/Fe3O4   |
| LD slag          | 100-300                  | 0.012                               | CaO, Ca <sub>2</sub> SiO <sub>4</sub> ,                             | Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> -                |
|                  |                          |                                     | Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>                      | CaFe <sub>3</sub> O <sub>5</sub>                                |
| Iron sand        | 100-300                  | 0.013 <sup>b</sup>                  | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> ,   | Fe <sub>2</sub> O <sub>3</sub> - Fe <sub>3</sub> O <sub>4</sub> |
|                  |                          |                                     | Fe <sub>2</sub> SiO <sub>4</sub>                                    |   |
| ZrO <sub>2</sub> | 100-200                  | 0 <sup>c</sup>                      | ZrO <sub>2</sub>  | -   |

<sup>a</sup> Values obtained at 950 °C.

 $^{\rm b}$  New value determined through TGA analysis with 5 %  $\rm H_2$  with the method used in previous work [30].

 $^{c}\,$  Confirmed with 5 %  $H_{2}$  with TGA analysis.

 $^{\rm d}\,$  Transformed to  $\rm Mn_3O_4$  in the used oxygen carrier.

#### Table 2

Proximate, ultimate and ash composition analysis of the *Spirulina* microalga (asreceived basis).

| Proximate (%) |                   | Ultin           | nate& Cl (%) | Ash composition (mg/(kg fuel)) <sup>d</sup> |        |  |  |  |  |
|---------------|-------------------|-----------------|--------------|---|--------|--|--|--|--|
| Moisture      | 17.8 C            |                 | 40.4         | Са  | 1465   |  |  |  |  |
| Ash           | 8.1               | Н               | 7.2          | K   | 17,267 |  |  |  |  |
| Volatiles     | 63.3              | Ν               | 8.9          | Mg  | 2856   |  |  |  |  |
| Fixed carbon  | 10.8 <sup>a</sup> | S               | 0.6          | Na  | 10,761 |  |  |  |  |
| LHV(MJ/kg)    | 18                | Ob              | 34.7         | Р   | 8298   |  |  |  |  |
|               |                   | C1 <sup>c</sup> | 1.04         | Si  | 728    |  |  |  |  |

<sup>a</sup> by the difference: 100-(moisture+ash+volatiles).

<sup>b</sup> By the difference: 100-(C + H + N + S + A).

<sup>c</sup> Analyzed with Ion Chromatography (IC).

<sup>d</sup> Analyzed with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The reactor tube is circular and made from high temperature steel, and it is 55 mm wide and 700 mm long. At the place of 300 mm above the tube bottom, there is a gas distributor, and well under the distributor is the preheating zone. The whole tube is placed inside an electric furnace which can heat up the reactor to temperatures of as high as 1200 °C. The bed temperature is measured with a K-type thermocouple and the pressure drop is monitored with a U-shaped pressure meter. On top of the reactor, there is a solid-fuel injection system, which has three valves (v1, v2 and v3), a fuel chamber between v1 and v3, and a pressure gauge (P). Below v3 is a long fuel chute which is inserted into the lower bed zone. The fuel is filled into the chamber through v1. The fuel chamber is pressurized to a gauge pressure of 0.1 MPa with N<sub>2</sub> entering via v2, and then the fuel is injected to the reactor by quick open-and-close of valve v3. The reactor exit is located at the reactor top. There are two filters and a condenser at the downstream of the reactor exit and were used to remove fines and water before the gas is sent to analysis.

#### 2.3. Experiment matrix

Two sets of experiments were conducted in the batch reactor. The first set is the materials activation/stabilization with cycles using CO (mixed either in 10 %CO + 25 %CO<sub>2</sub> + 65 %N<sub>2</sub> or 18 %CO + 23 %CO<sub>2</sub> + 59 %N\_2) in reduction and 10 %O\_2 + 90 %N\_2 in oxidation. In the case of ilmenite and MnGBhne, which have a high oxygen content, the gas with 18 %CO is used to lower the time needed for reduction, and in the case of LD slag and iron sand the 10 %CO is used. All the activation/ stabilization experiments were conducted at 900 °C using 400 g oxygen carriers. During the cycles, the ilmenite reactivity increases, i.e., the material is activated, whereas the LD slag, MnGBhne and iron sand experience decrease of reactivity during cycles. The activity change of oxygen carriers with cycles depends on many physical and chemical factors (microstructure, chemical composition, etc.) and the reason behind is not fully understood. Therefore, for a new material, its reactivity change with cycles cannot be foreseen and experimental tests should be done to confirm it.

In the second set of experiments, the oxygen carriers above are used. In this set, the bed mass was kept at 200 g which has either only oxygen carriers or a mixture of an oxygen carrier and  $ZrO_2$  with weight ratios of 80/120 and 60/140 as depicted in Table 3 below. The mixing with  $ZrO_2$  is to study the effect of oxygen carrier and its conversion on the gasification performance. The available amount of oxygen in the bed determines the oxygen to fuel ratio, and thus can also affect the final char conversion. Given this fact, a methodology was implemented to keep the oxygen amount in the bed the same. With this method, the fully oxidized bed is first exposed to a controlled reduction with either 10 % CO or 18 % CO (as seen above) under certain reduction time. Based on the reduction time and CO flow, the amount of available oxygen over the total oxygen in the oxygen is calculated, and thus named as desired oxidation degree ( $X_{ox,des}$ ) which has values slightly different as compared to the real oxidation degree ( $X_{ox}$ ), as seen in Table 4 below.



Fig. 2. XRD pattern and main phases of the microalgae char.



Fig. 3. Setup of the batch fluidized bed reactor.

After the controlled reductions, the  $X_{ox,des}$  is 0.2 for the case with 200 g oxygen carriers, 0.5 for the 80/120 mixture and 1 for the 40/160 mixture. Therefore, the available oxygen is kept at around 1.5 g for ilmenite, 2 g for MnGBhne, 0.5 g for LD slag and 0.5 g for iron sand in all the tests. With this, we can evaluate the effect of the oxygen carrier conversion on the char gasification rate while ruling out the effect of overall oxygen-to-fuel ratio. The pre-reduced oxygen carriers are then used in the following gasification experiments, using 40 %H<sub>2</sub>O + 60 % N<sub>2</sub> as reactant and fluidizing gas and using 2 g microalgae as fuel. After the gasification step, the bed is exposed to oxidation with 10 %O<sub>2</sub> + 90 %N<sub>2</sub>. In addition, steam gasification with only 200 g ZrO<sub>2</sub> in the bed was carried out to compare with those with presence of oxygen carriers. All

the experiments in the second set were conducted at three typical temperatures (850, 900 and 950 °C). The inlet gas was kept at a total flow of 300 Ln/h at the STP condition, and the corresponding gas velocity at 900 °C was around 0.15 m/s. The gas concentration was analyzed with three analyzers (H<sub>2</sub> by SIDOR Sick Maihak, and CO, CH<sub>4</sub> and CO<sub>2</sub> by Siemens Ultramat 23 and O<sub>2</sub> by Oxymat 5E) and the data was logged with a rate of one data per second. The uncertainty of gas concentration is  $\pm 2$  % for H<sub>2</sub>,  $\pm 0.2$  % for CO,  $\pm 1$  % for CO<sub>2</sub>,  $\pm 0.25$  % for CH<sub>4</sub> and  $\pm 1.25$  % for O<sub>2</sub>. Following the complete of each experimental campaign, the bed was oxidized and cooled down in air to room temperature and then bed samples were taken for characterizations.

### 3. Data processing

The oxidation degree of oxygen carrier was controlled by doing a partial reduction of the fully oxidized oxygen carrier. However, this value was calculated with the data from the oxidation period of the pre-reducing-oxidation cycles, because there the gas composition (only  $O_2$  and  $N_2$ ), integration and mass balance are much simpler than the reduction (CO, CO<sub>2</sub>, and N<sub>2</sub>). Therefore, the propagation error for data processing is smaller than with the data from the reduction period [50,51]. Moreover, because there is no carbon deposition in the reduction, the oxygen consumed by the oxygen carrier in oxidation is equal to the oxygen amount taken by CO in the pre-reduction. Therefore, the oxidation degree  $X_{ox}$  is obtained with Eq. (1).

$$X_{\rm ox} = 1 - \frac{M_{\rm O} \int\limits_{t_0}^{t_{\rm end}} (x_{{\rm O}_{2,\rm in}} F_{\rm in,ox} - x_{{\rm O}_{2,\rm out}} F_{\rm out,ox}) dt}{R_{\rm oc} m_{\rm oc}}$$
(1)

where  $M_{\rm O}$  is the molecular weight of oxygen atom (16 g/mol),  $x_{\rm O2,in}$  and  $x_{\rm O2,out}$  are the oxygen concentrations in the gases entering and leaving the reactor.  $F_{\rm in}$  and  $F_{\rm out}$  are total gas molar flows (mol/s) at the entry and exit of the reactor. The  $t_0$  represents the start time of reaction and  $t_{\rm end}$  is the end time of reaction. The  $t_0$  was estimated with pulses of O<sub>2</sub> injected to the reactor and the  $t_{\rm end}$  was the time when the O<sub>2</sub> reached 21 %.  $R_{\rm OC}$  is the oxygen transport capacity (see Table 1) of oxygen carrier and  $m_{\rm OC}$  the mass (g) of oxygen carrier in the bed.

The  $F_{\text{out,ox}}$  is calculated using the N<sub>2</sub> flow which is the same at the reactor inlet and outlet during the oxidation. The inlet N<sub>2</sub> flow is obtained through multiplying the nitrogen concentration (1- $x_{\text{O2,in}}$ ) by the

Table 3

A summary of the experiments with the four oxygen carriers and ZrO<sub>2</sub> as bed.

| Oxygen carrier                        | OC/ZrO <sub>2</sub> ratio            | 200/0 (Desired $X_{ox,des} = 0.2^*$ ) | $80/120$ (Desired $X_{ox,des} = 0.5^*$ ) | $40/160$ (Desired $X_{ox,des} = 1^*$ ) | 0/200         |
|---------------------------------------|--------------------------------------|---------------------------------------|--|--|---------------|
|                                       | Pre-treatment                        |                                       |  |  |               |
| Ilmenite                              | Activated in previous work [43,44]   | 850, 900, 950                         | 850, 900, 950                            | 850, 900, 950                          |               |
| MnGBhn                                | Stabilization** @900                 | 850, 900, 950                         | 850, 900, 950                            | 850, 900, 950                          |               |
| LD slag                               | Calcination, then Stabilization @900 | 850, 900, 950                         | 850, 900, 950                            | 850, 900, 950                          |               |
| Iron sand                             | Calcination, then Stabilization @900 | 850, 900, 950                         | 850, 900, 950                            | 850, 900, 950                          |               |
| ZrO <sub>2</sub> -H <sub>2</sub> O*** |                                      |                                       |  |  | 850, 900, 950 |

 $^{*}$  Desired oxidation degrees according to theoretical calculation during the pre-reduction with CO + CO<sub>2</sub> mixture and the corresponding real oxidation degrees are in Table 4.

\*\* The stabilization means till cycles when there are no more changes of the gas concentration at reactor exit.

\*\*\* Blank gasification tests.

#### Table 4

|  | Гh | e oxidation | degree | $(X_{ox})$ | of al | l the o | xygen | carriers | after | controlled | l reductio | ons as | s compared | l to | the | desired | oxidati | on d | legree | $(X_{\text{ox de}})$ | ۵. |
|--|----|-------------|--------|------------|-------|---------|-------|----------|-------|------------|------------|--------|------------|------|-----|---------|---------|------|--------|----------------------|----|
|--|----|-------------|--------|------------|-------|---------|-------|----------|-------|------------|------------|--------|------------|------|-----|---------|---------|------|--------|----------------------|----|

|        |                                    | ilmenite     |              |           | MnGBhr       | ne           |           | LD slag      |              |           | iron sand    | 1            |           |
|--------|------------------------------------|--------------|--------------|-----------|--------------|--------------|-----------|--------------|--------------|-----------|--------------|--------------|-----------|
| Т      | Desired X <sub>ox,des</sub>        | 0.2          | 0.5          | 1         | 0.2          | 0.5          | 1         | 0.2          | 0.5          | 1         | 0.2          | 0.5          | 1         |
| 850 °C | $X_{\rm ox}$                       | 0.22         | 0.54         | 1         | 0.30         | 0.57         | 1         | 0.33         | 0.56         | 1         | 0.27         | 0.50         | 1         |
| 900 °C | $X_{ox}$                           | 0.21         | 0.45         | 1.48      | 0.27         | 0.49         | 2.00      | 0.25         | 0.50         | 0.48      | 0.20         | 0.32         | 1         |
| 950 °C | Available O (g)<br>X <sub>ox</sub> | 1.55<br>0.22 | 1.33<br>0.43 | 1.48<br>1 | 2.70<br>0.27 | 1.96<br>0.43 | 2.00<br>1 | 0.60<br>0.21 | 0.48<br>0.44 | 0.48<br>1 | 0.52<br>0.17 | 0.51<br>0.52 | 0.52<br>1 |
|        | Available O (g)                    | 1.63         | 1.27         | 1.48      | 2.70         | 1.72         | 2.00      | 0.50         | 0.42         | 0.48      | 0.44         | 0.54         | 0.52      |

inlet total flow.

$$F_{\text{out,ox}} = \frac{F_{\text{in,ox}}(1 - x_{\text{O}_{2,\text{in}}})}{1 - x_{\text{O}_{2,\text{out}}}}$$
(2)

During the microalgae gasification, the oxygen transferring rate ( $r_0$ ) to the fuel gasification can be calculated by considering the oxygen balance between the inlet and outlet of the reactor, as seen in Eq. (3) below. The  $F_{\text{out,red}}$  in Eq. (3) below was calculated based on a similar N<sub>2</sub> balance as described in Eq. (2), but with the gases during the reduction period. And  $x_{\text{CO2}}$ ,  $x_{\text{CO}}$  and  $x_{\text{H2}}$  are the concentrations of CO<sub>2</sub>, CO and H<sub>2</sub> in the gasification period.

$$r_{\rm O} = F_{\rm out, red} (2x_{\rm CO_2} + x_{\rm CO} - x_{\rm H_2})$$
(3)

The rate of carbon generation is determined with the sum of the flows of all carbonaceous gases (with concentrations of  $x_{CO2,out}$  and  $x_{CO,out}$ ) during the gasification step.

$$r_{\rm C} = F_{\rm out, red} \left( x_{\rm CO_{2,out}} + x_{\rm CO_{out}} \right) \tag{4}$$

The char conversion  $(X_{Char})$  can be calculated by dividing the instantaneously accumulated carbon amount over the total carbon accumulation during the gasification.

$$X_{\text{Char}} = \frac{\int\limits_{t_0}^{t} r_{\text{C}} dt}{\int\limits_{t_0}^{t_{\text{end}}} r_{\text{C}} dt}$$
(5)

The instantaneous gasification rate ( $r_{inst,gasif}$ ) is obtained based on the residual char amount in the bed according to the simplified model in Eq. (6) below.

$$r_{\rm inst,gasif} = \frac{1}{1 - X_{\rm Char}} \frac{dX_{\rm Char}}{dt}$$
(6)

The instantaneous gas yield  $Y_i$  for CO (i = CO) and H<sub>2</sub> ( $i = H_2$ ) from char gasification is also taken into account when evaluating the performance in char gasification period. The average CO and H<sub>2</sub> yield ( $Y_{i}$ , ave) were taken when limiting the  $X_{Char}$  in the range of 0.3–0.7 for evaluation.

$$Y_i = \frac{x_i}{x_{\rm CH_4} + x_{\rm CO_2} + x_{\rm CO}}$$
(7)

To facilitate the comparison with beds, the dry gas concentrations ( $x_{CO}$ ,  $x_{CO2}$ ,  $x_{H2}$  and  $x_{CH4}$ ) measured with the gas analyzers during gasification were then converted to N<sub>2</sub>-free concentrations ( $x_{i,N2-free}$ ) with the equation below.

$$x_{i,N_2-free} = \frac{x_i}{x_{CH_4} + x_{CO_2} + x_{CO} + x_{H_2}}$$
(8)

#### 4. Results

#### 4.1. Typical reaction progress

Fig. 4 describes a typical concentration profile for different gases in a common test which is composed by two prereductions with CO, a gasification with steam and two oxidations with air. The first reduction with CO was made to find a reaction time which can reduce the oxygen carrier to a predefined oxidation degree, i.e., to control the value of  $X_{ox}$  (in this case is equal to 0.21) which is calculated with Eq. (1). Once a suitable prereduction time is found, it is then used in the second CO reduction to maintain the same  $X_{ox}$  value prior to the microalgae gasification step.

Immediately after the second CO reduction, the fluidization gas was quickly switched to steam (at around 69 min in Fig. 4) to establish a gasification atmosphere. When the gas was switched to steam, H<sub>2</sub> was found at the reactor exit, and then the concentration started to increase gradually to a peak of around 1 % in the specific case shown in Fig. 4. The hydrogen can be attributed to the water splitting process shown in reaction (*r7*). This was observed for all the four oxygen carriers, and is discussed in the Supporting Information. The H<sub>2</sub> generation means that some FeO and/or Fe were formed during the CO reduction stage, which could be oxidized to Fe<sub>3</sub>O<sub>4</sub> or FeO by steam meanwhile generating H<sub>2</sub>.

$$Fe/FeO + H_2O \rightarrow FeO/Fe_3O_4 + H_2$$
 (r7)

In addition to  $H_2$  generation, LD slag has some  $CO_2$  release and CO generation during the  $N_2$  purge period just after the CO reduction, as seen in the Supporting Information. This can be attributed to the CaCO<sub>3</sub> decomposition to CaO and an immediate splitting of the CO<sub>2</sub> with



**Fig. 4.** Prereduction tests with CO (first CO reduction) to determine the condition needed for reaching a certain reduction degree of the bed, and the second CO reduction starts the real prereduction-gasification and oxidation cycle. The gasification step starts when 2 g *Spirulina* microalga is injected. The curve is from a test at 900 °C with 200 g ilmenite ( $X_{ox} = 0.21$ ). The periods not labelled are the sweepings with N<sub>2</sub>.

presence of Fe or FeO in the reduced LD slag, as described in reactions (*r8*) and (*r9*).

gasification rate, and this is centrally focused when there is negligible effect of the oxygen-to-fuel ratio.

$$CaCO_3 \leftrightarrow CaO + CO_2$$
 (r8)

 $Fe/FeO + CO_2 \rightarrow FeO/Fe_3O_4 + CO$  (r9)

After a period of stabilization in steam atmosphere, 2 g microalgae are injected to the reactor to start the gasification process, see the "gasification" segment in Fig. 4. The gasification starts with a rapid volatiles release and the volatiles may react with oxygen that entered through fuel injector (explained in Section 4.2 below) as well as the oxygen carrier bed, thus peaks of CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> are observed in the first seconds (at around the 71st min). Although the char gasification may occur simultaneously with the devolatilization, we divide the volatiles release and char gasification with the vanishing time of the CH4 concentration. This is to facilitate the analysis of different reaction behaviours of volatiles and char. With this in mind, we consider that at the 73rd min the devolatilization completed and the gasification started. The devolatilization and gasification took around 8 min. The last oxidation was used to re-oxidize the bed for use in the next cycle, and no CO2 was found during the oxidation. This means the microalgae are all gasified during the gasification step.

The oxidation degree (Xox) of the oxygen carriers after the CO prereduction is summarized in Table 4 and compared with the desired values (X<sub>ox.des</sub>). As seen in the table, the desired oxidation degrees and the available oxygen in the bed are difficult to reach with the prereductions, because the exact time needed is not known and many tests are needed to approximate the time. But the real oxidation degree Xox and available oxygen are close to the desired values for all the oxygen carriers at the three temperatures, and the difference is mostly lower than 15 %, except for several points with low oxidation degrees (Xox,des = 0.2) that are hard to control during the prereductions. The difference is mostly acceptable when considering the uncertainty of gas measurement and the uncertainty of reaction time estimation with pulses of O2 as stated in Section 3 above. With this, the available oxygen in the bed for all the cases studied is similar for the same oxygen carrier and there is small effect of oxygen-to-fuel ratio. Also, selecting suitable conditions for different oxygen carrier will offer information about the relevance of the oxygen carrier properties (other than reactivity) on the char

#### 4.2. Evolution of volatiles

Fig. 5 below displays the N<sub>2</sub>-free gas concentrations from volatiles conversion when using ZrO<sub>2</sub> and ilmenite as the bed at 900 °C. In both cases, there is a first peak of CO<sub>2</sub> at around 5–15 s, and this could be caused by volatiles combustion with a small amount of air from the tube between valves v1 and v3, cf. Fig. 3 above. This small amount of air entered the tube between v1 and v3 when the v1 was opened to add the microalgae, and this air ingress was not able to avoid with the current fuel feeding system. When the air is consumed completely, the volatiles components CH<sub>4</sub> and H<sub>2</sub> start rising, and CO and CO<sub>2</sub> are also seen because they are also volatiles components and can be also generated from CH<sub>4</sub> reforming due the presence of steam in the reactor. Comparing the ilmenite bed with the ZrO<sub>2</sub> bed, there are slightly more CO<sub>2</sub>, and slightly less H<sub>2</sub> and CO with the ilmenite. This indicates that the volatiles have some contact with the oxygen carriers but the contact might be very low, and so the information could be used for the volatiles assessments is little. Therefore, below we focus mainly on the char gasification.

#### 4.3. Char gasification with ZrO<sub>2</sub>

As discussed before, the char gasification -reactions (r2) and (r3)- is assumed to start after CH<sub>4</sub> vanishes, and Fig. 6 shows the dry and N<sub>2</sub> free gas concentrations in the gasification with the ZrO<sub>2</sub> bed. The main gases from gasification are CO, CO<sub>2</sub> and H<sub>2</sub>, and it is noted that the CO<sub>2</sub> and H<sub>2</sub> have a close concentration. This suggests the Water Gas Shift (WGS) -reaction (r10)- was relevant, as this reaction favours the generation of similar amount of CO<sub>2</sub> and H<sub>2</sub>, which can be expected because a high H<sub>2</sub>O concentration was used in the experiments. At around 320 s in Fig. 6, a relatively big difference between the CO<sub>2</sub> and H<sub>2</sub> concentrations is observed, and this can be attributed to the gas measurement errors as a result of low gas concentrations when the gasification is close to the end of reaction. Fig. 6 also compares the results with literature data from fixed-bed experiments with *Chlorella vulgaris* and particles of silica [15]. Because of different experimental conditions (microalgae type, steam



Fig. 5. N<sub>2</sub>-free gas concentrations during the volatiles release from the 2 g microalgae in steam with (A) 200 g ZrO<sub>2</sub> as bed and (B) a mixture of 40 g Ilmenite and 160 g ZrO<sub>2</sub> as bed at 900 °C.



**Fig. 6.** N<sub>2</sub>-free gas concentrations in the gasification step with 2 g microalgae at 900 °C with 200 g ZrO<sub>2</sub> as bed. Data presented in dots are *Chlorella vulgaris* with silica and are adapted from literature [15] for comparison. Colours show the different gases (yellow for H<sub>2</sub>, red for CO<sub>2</sub>, blue for CO and green for CH<sub>4</sub>). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration, temperature, oxygen-to-fuel ratio, etc.) and reactor type, the literature data is different as compared to our results. But the tendency of the change of gas concentrations is the similar, and the CO concentration is close in both cases. Further, the gas distribution in CLG with microalgae is quite as compared to normal air gasification presented in literatures [52–54]. However, the CLG process has the advantages of inherently avoiding ash fouling to the heat-exchanger that normal gasification doesn't have.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (r10)

#### 4.4. Gasification with oxygen carriers

Fig. 7A, B displays the gas concentrations during the gasification with the presence of 80 g ilmenite, MnGBhne, LD slag and iron sand that have been half-reduced (X $_{ox}$  = 0.5) at 900 °C. In comparison to the ZrO<sub>2</sub> bed, the WGS equilibrium which generates equal CO<sub>2</sub> and H<sub>2</sub> was not reached with presence of the oxygen carriers. In the case of ilmenite and MnGBhne, the main product gas is  $CO_2$  while  $H_2$  and CO are much lower. This is because there is available oxygen in the ilmenite and MnGBhne carriers and the oxygen can convert the gasification intermediates (CO and H<sub>2</sub>) to CO<sub>2</sub> and H<sub>2</sub>O. Different to ilmenite and MnGBhne, the LD slag and iron sand, however, have H<sub>2</sub> as the main gas, and CO<sub>2</sub> is hugely suppressed due to the lower available oxygen in these oxygen carriers. Fig. 7A, B compares the gas profiles with literature [15], and it can be seen that the current work has a lower H<sub>2</sub> with ilmenite and MnGBhne and a higher H<sub>2</sub> with LD slag and iron sand as compared to the literature using ferric oxide with Chlorella vulgaris in a fixed bed [15]. The CO concentration in the current work is lower than the values in the literature, and this could be attributed to better conversion in fluidized bed.

Fig. 7C compares the instantaneous char gasification rate with the use of different bed materials (ZrO2, ilmenite, MnGBhne, iron sand and LD slag). In the case of ZrO<sub>2</sub>, the gasification rate is around 25 %/min and relatively constant until X<sub>char</sub> is around 0.7. The gasification rate when X<sub>C</sub> is higher than 0.7 is uncertain as it is close to the end of gasification and the error in gas concentration is high. The use of ilmenite and MnGBhne improves the gasification rate to 45-60 %/min, while these are further increased to 100-150 %/min with LD slag and iron sand. When comparing with the literature's data [15], the Chlorella vulgaris gasification is 10 %/min faster than the Spirulina used in current work, but the information given in the literature is not sufficient for us to analyze the reason behind. As a summary, the LD slag and iron sand have the highest gasification rate among the four oxygen carriers. Notably, these higher char gasification rates were obtained under conditions that have higher H<sub>2</sub> concentration than with ilmenite and MnGBhne, which is an inhibitory compound for steam gasification. The



**Fig. 7.** (A, B) N<sub>2</sub>-free gas concentrations during the microalgae gasification with (A) ilmenite (solid lines) and MnGBhne (dashed lines) and with (B) LD slag (solid lines) and iron sand (dashed lines), the dots are literature data [15] and are presented for comparison and (C) the instantaneous gasification rate for the four oxygen carriers as compared to the 200 g  $ZrO_2$  bed. Data with oxygen carriers are from the gasification with the 80 g oxygen carrier +120 g  $ZrO_2$  mixture ( $X_{ox,des} = 0.5$ ) at 900 °C.

significantly different behaviour with LD slag and iron sand as compared to ilmenite and MnGBhne could be attributed to several reasons, such as the catalytic effect on gasification and calcium enhancement, and these are discussed below in Section 5.

Fig. 8 displays the average char gasification rate at 850, 900 and 950 °C with oxygen carriers that have been pre-reduced to different X<sub>ox</sub> values (see Table 4). Obviously, the increase of temperature promotes the gasification because of faster reaction kinetics. A higher oxidation degree (X<sub>ox</sub>) of the oxygen carriers improves the rate of gasification with LD slag and ilmenite while showing irregular effect with iron sand, but the oxidation degree has a trend of lowering the gasification rate with MnGBhne. The available oxygen in the bed is relatively constant for each oxygen carrier, except MnGBhne because the Xox is close to 0.3 and higher than the  $X_{ox,des}$  (0.2), and the available oxygen in the bed is 1 g more than the desired 2 g, as seen in Fig. 8 and Table 4. The fact that the ilmenite and MnGBhne have much more available oxygen than the iron sand and LD slag at all the X<sub>ox</sub> means more available oxygen in the bed. This is supposed to lead to a faster gasification than iron sand and LD slag. However, the latter actually have the highest gasification rate among the oxygen carriers. Therefore, the high gasification rates with LD slag and iron sand might be because of other reasons which are discussed in Section 5.

Fig. 9 presents the average CO and H<sub>2</sub> yield in the gasification process with the four oxygen carriers and ZrO<sub>2</sub>. When using the ZrO<sub>2</sub> as inert bed, the average H<sub>2</sub> yield (Y<sub>H2,ave</sub>) and CO yield (Y<sub>CO,ave</sub>) are relatively constant at all the three temperatures, and this phenomenon aligns well with the definition of gas yield in Eq. (7). The much lower CO yield than H<sub>2</sub> yield could be a result of strong water-gas shift (WGS) as described in reaction r10 above. With presence of oxygen carriers, the CO and H<sub>2</sub> gas yield has bare effects from reactor temperature, but the sum  $Y_{H2,ave} + Y_{CO,ave}$  is different with different oxygen carriers; higher with the iron sand and LD slag as compared to the ilmenite and MnGBhne, which could be because the lower reactivity with CO and H<sub>2</sub> of the former as compared to the latter [55,56]. In addition, the H<sub>2</sub> yield is higher and CO yield is lower with LD slag as compared to iron sand, and this suggests the LD slag may have a stronger enhancement on the WGS equilibrium (r10) towards the direction for H<sub>2</sub> generation. The increase of oxidation degree of the oxygen carriers seems favourable for the generation of more CO and less H<sub>2</sub>.

Fig. 10 below brings together and compares three key indicators relevant for the process, that is, the oxygen transfer rate ( $r_0$ ), H<sub>2</sub> concentration ( $x_{H2}$ ) and gasification rate ( $r_{inst,gasif}$ ). A higher value of  $r_0$  means a faster oxygen transfer for the microalgae conversion. According to the data presented in Fig. 10, LD slag and iron sand have the lowest



Fig. 8. Effect of oxygen carrier oxidation degree ( $X_{ox}$ ) and temperature (850, 900 and 950 °C) on the average instantaneous gasification rate (left Y axis). The available oxygen amount in the bed of different oxygen carriers is shown on the right Y axis.



Fig. 9. Average H<sub>2</sub> and CO yield (Y<sub>CO,ave</sub> and Y<sub>H2,ave</sub>) with the four oxygen carriers (solid lines) and ZrO<sub>2</sub> (horizontal-dashed lines) at 850, 900 and 950 °C.



Fig. 10. Comparison of oxygen transfer rate ( $r_0$ ), H<sub>2</sub> concentration and the instantaneous gasification rate ( $r_{inst,gasif}$ ) for the four oxygen carriers with the three desired oxidation ( $X_{ox,des}$ ) degrees at 900 °C.

oxygen transfer rate and the highest H<sub>2</sub> concentration which could lead to a slower gasification. More indeed, the H<sub>2</sub> concentration with LD slag and iron sand is around 1.5–2 times that with ilmenite and MnGBhne. When considering a Langmuir–Hinshelwood type rate expression, the inhibition with 1.5–2 times higher H<sub>2</sub> concentrations could result in a gasification with a rate of 1/2–2/3 of the original values [57]. However, conversely, the use of LD slag and iron sand resulted in a 1.5–2 times faster gasification, which is the highest among the four oxygen carriers. The enhanced gasification with LD slag and iron sand is even more clearly seen in the case with high oxidation degrees (X<sub>ox,des</sub> = 0.5 and X<sub>ox,des</sub> = 1), as compared to the case of a lower oxidation degree (X<sub>ox,des</sub>)

= 0.2). Therefore, the LD slag and iron sand can promote the microalgae gasification, and their low oxygen transfer rate doesn't slow down the gasification. Actually, the gasification also relies on the oxygen transfer from the gasifying agent, which is steam in the present work. And the oxygen transfer from oxygen carrier probably makes changes to the gas yield in the product, namely  $H_2$  and CO conversion to  $H_2O$  and  $CO_2$ . The higher syngas yield from the LD slag and iron sand may not rely highly on the oxygen transfer rate and other mechanisms are discussed in Section 5.

Thus, the effect of the oxygen carrier reactivity on the gas yield is low. Notably, the oxygen transferred to the fuel reactor may be easily controlled by modifying the air flow fed to the air reactor in a CLG plant. Then, the oxygen carrier reactivity has low influence on the oxygen transfer in CLG, unless the oxygen carrier has very poor reactivity which is however not the case in many pilot tests [58,59]. However, the gasification rate is of high relevance on the CLG performance. In a CLG unit, the char should be gasified through reactions (*r*2) and (*r*3) to avoid its bypass to the air reactor where it would be burnt via reaction (*r*6). To maximize the carbon confinement in syngas, the carbon conversion in the fuel reactor ( $\eta_{\rm CC}$ ) should be as high as possible, which depends on the fraction of carbon as fixed carbon in the fuel ( $f_{C,fix}$ ) and the char conversion ( $X_{char}$ ) [58].

$$\eta_{CC} = f_{C,vol} + f_{C,fix} X_{char} = 1 - (1 - X_{char}) f_{C,fix}$$
(9)

The char conversion is a function of the reactivity of the fuel and the operating conditions, mainly temperature, fuel residence time in the fuel reactor and the type of gasifying agent [59]. However, the present work reveals that the oxygen carrier itself may affect the gasification rate. And the use of LD slag and iron sand has a faster char gasification. Thus, using LD slag and iron sand is promising in improving the char conversion in the fuel reactor in a large CLG system, and this can reduce the fraction of carbon emitted as  $CO_2$  from the air reactor.

#### 4.5. Oxygen carrier characterization

#### 4.5.1. XRD phase

As mentioned before in Section 2.1, before the current work the ilmenite has been used in a previous campaign with biomass, so the ilmenite has already been activated and its phase has been stabilized to Fe<sub>2</sub>TiO<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, see the XRD pattern in Fig. 11 below. The LD slag, iron sand and MnGBhne were only calcined and sieved before using in the current work. Based on the XRD analysis, the used ilmenite, LD slag and iron sand have the same XRD phases as compared to the fresh oxygen carriers, see Fig. 11. But in the case of MnGBhne, the Mn<sup>3+</sup> in the form of bixbyite (FeMnO<sub>3</sub>) in the fresh particles was transformed to Mn<sup>8/3+</sup> in the form of Mn<sub>3</sub>O<sub>4</sub> after the use in experiments, and this is because of the FeMnO<sub>3</sub> cannot be restored with typical O<sub>2</sub> concentrations and temperatures for chemical looping processes, see Mei et al. [30]. Alkali-oxygen carrier interactions that are frequently reported

with other oxygen carriers [33,60,61], and are seen with the ilmenite in previous campaign [43,44]. However, the ash-oxygen carrier interactions are not found with the XRD analyses. This could be attributed to the small numbers of cycles where alkalis' retention in the oxygen carrier is low and lower than the instrument detection limit. Another possibility is the alkalis are in the form of amorphous phases which could not be identified with the XRD technique.

#### 4.5.2. SEM-EDX

As the ilmenite has been used with biomasses in previous campaign with the 20 kW<sub>th</sub> pilot at the ICB-CSIC group [43,44], it has been well aged and thus has a clear shell enriching iron due to the iron-outward transmission from the oxygen carrier particle bulk [43,44,62], see Fig. 12 below. Meanwhile, the biomass-alkalis have strong interactions with the oxygen carrier; the potassium penetrated and mainly concentrated in the core of the oxygen carrier whereas the calcium is mainly on the ilmenite particles surface. After use in the batch reactor, the morphology and element distribution of the ilmenite remained the same as compared to the particles from the 20 kW experiments [43,44], as seen in the Fig. 12. The MnGBhne was not used in other processes before the present work, and it became more porous after the batch reactor experiments as compared to the fresh particles (Supporting Information). In addition, the EDX analyses show that the elements are relatively uniform in the used MnGBhne oxygen carrier. In the case of LD slag, both the fresh and used particles have some fines, but the used LD slag has less fines than the fresh material, as seen in Fig. 12 and the Supporting Information. The LD slag particles have calcium, iron and silicon as the main element, and the calcium is relatively even distributed in the particles whereas the other elements' distribution in the oxygen carrier is very uneven. There are Fe-rich areas and Si-rich areas in a particle, while the Ca is found in most particles (Fig. 12-C5). The Fe and Si are closely linked, and generally distributed in spots which are surrounded by the bulk material. The iron sand particles have a well-sintered surface and good integrity before and after use in the batch reactor tests, and some particles are spherical. Fe and Si are well distributed in the particles and the other elements distribution are very similar before and after use in the batch experiments, see the Supporting Information.

We also studied the element distribution with EDX point-analyses on



Fig. 11. XRD phases in the oxygen carriers before (in green colour) and after (in grey colour) use in the current work. The same phases found before and after use are marked with black labels, and the unique phases are marked with the same colour with the raw pattern, i.e., the phase found only in the oxygen carrier before use is labelled in green and the phase found only in the used material is labelled with grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 12.** Morphology and EDX mapping analyses of the ilmenite (A1-A6), MnGBhne (B1-B6), LD slag (C1-C6) and iron sand (D1-D6) after the batch-reactor experiments. The images in the A1-D1 row are morphology of the bulk particles, in the A2-D2 row are for the particles' cross-section. The images A3, A4, A5 and A6 present the Fe, Ti, K and Ca distribution in the cross-section of ilmenite. The B3, B4, B5 and B6 are for Fe, Mn, K and Si on MnGBhne cross-section. C3, C4, C5 and C6 are Fe, Si, Ca and Al for the LD slag cross-section and D3, D4, D5 and D6 are Fe, Si, Ca and Al distribution on the iron sand cross-section.

the surface of typical oxygen carrier particles, as presented in Fig. 13 below. The ilmenite surface shown in Fig. 13A has dark and bright regions. Based on the EDX analyses, the dark region is rich in calcium (31

% Ca, see point I) which is from the biomasses in the previous 20 kW<sub>th</sub> campaign [43,44] and the bright region is iron-dominant (41 % Fe, see point II). On the surface of the used MnGBhne presented in Fig. 13B, the



Fig. 13. EDX point analyses of the surface of the used (A) ilmenite (B) MnGBhne (C) LD slag and (D) iron sand. The "+" indicates where the point EDX analyses were made, and the I and II are the two points analyzed for each sample. The data are the atomic percentage (at.%) of each element. The bottom-left panel in (C) presents the surface of a fine particle and the composition is displayed. The top-right panel in (D) shows the whole particle where the image (D) was taken.

distribution of Mn and Fe is relatively even, and there are small amount of Si, Al and K. These elements have a similar amount as compared to the values obtained with the ICP-AES analyses with the bulk particles, see previous work by Mei et al. [30]. This means the MnGBhne has a relatively homogeneous composition, which is consistent with the SEM-EDX analysis as presented in Fig. 12 above. The LD slag surface has some fines, as seen in Fig. 13C, and the surface has Ca, some Fe and some Si as the main elements. In addition, the LD slag fines have similar composition as compared to the bulk surface, see the bottom-left panel of Fig. 13C. The iron sand surface has mostly iron and silicon, but we also found some sites with significant amount of calcium, for example on the spherical particle surface as shown in Fig. 13D where a "palp" grows outward the particle. The "palp" has 41 % Fe and 14 % Ca which is different to the particle bulk that has only 1 % Ca. Therefore, although the calcium amount in the iron sand is not high, there are sites with a high Ca content on the surface.

#### 5. On the high performance of LD slag and iron sand

The high gas yield and gasification rate with LD slag and iron sand as compared to ilmenite and MnGBhne in the microalgae gasification can be attributed to several factors and hypotheses, as discussed below.

#### 5.1. Hypothesis of catalysis by calcium

Calcium is catalyst for char gasification, and to catalyze the gasification, calcium needs to have good contact with the char. The LD slag has a high calcium content and the iron sand has some calcium in the bulk particles and on the particle surface, cf Section 4.5.2. Furthermore, it is known the LD slag is easy to break down to fines and smaller particles [36] which also happened in the batch reactor, and the fines and smaller particles have significant amount of calcium cf Fig. 13 above. Fig. 14 illustrates how the oxygen carrier particles may break down and how the calcium may contact with the char. In static state, the calcium can stay inside the oxygen carrier and also on its surface. But after being fluidized, the particles collide with each other and friction with the reactor wall. In either case, particles can break to fines. So, there are chances to form Ca-dominant fines in the bed, and these Ca-rich fines can move to the bed surface. As in our batch reactor the fuel chute is inserted inside the bed, so when the char passes through the fuel chute and enters to the bed, it has a direct contact with the oxygen carrier particles and the fines that have high calcium content. Moreover, in fact the batch reactor is a bubbling fluidized bed, and this allows the microalgae char a slow rising to the bed surface, and thus there could be a sufficient reaction time. The unconverted char which moves to the bed surface still has chances to contact with Ca, as illustrated in Fig. 14. We analyzed the Ca content in the calcined and used LD slag and iron sand with ICP-AES technique, see Supporting Information. The results show that the Ca content was almost unchanged after use in the batch reactor, and this could be attributed to the homogeneous distribution of Ca in the LD slag and iron sand particles, c.f. Fig. 12 above. Therefore, the breaking-down of these particles didn't lead to significant changes in the element composition in the bulk bed particles. We cannot confirm the hypothesis only based on the bulk particles' ICP-AES analyses, and more studies (e.g., with long-time pilot tests) are needed.

#### 5.2. CO<sub>2</sub> sorption through carbonation

Carbonation through the CaO and CO<sub>2</sub> reaction -reverse reaction (*r8*)- takes up the CO<sub>2</sub> in the product gas generated from the gasification and the WGS shift reaction (*r10*), and this leads to direct increases of H<sub>2</sub> and CO concentrations and thus their yield in the product. Thermodynamically, the carbonation happens at temperatures lower than 800 °C, which means the carbonation may not happen in the main reacting zone which has a temperature of 850–950 °C, as seen in Fig. 15. However, above the main zone the temperature could be lower than 800 °C because there is no heating supply or sufficient insulation. Meanwhile, the fines containing calcium as described above could be transferred to this "colder" zone. Therefore, the carbonation can happen in the "colder" zone above the main reacting zone and thus leads to a higher H<sub>2</sub> and CO yield when using the LD slag and iron sand as bed materials.

#### 6. Conclusions

Ilmenite, LD slag, iron sand and MnGBhne manganese ore were tested as potential oxygen carriers with a *Spirulina* microalga for Chemical Looping Gasification (CLG) process. Series of experiments in a batch-fluidized bed reactor were done with the oxygen carriers with



Fig. 14. Proposed mechanism of oxygen carrier particles breaking down and the calcium contact with char and catalysis on the gasification of char when rising in the bed.



Fig. 15. Photo of the reactor and the reactor's preheating zone, reacting zone and an upper zone where the temperature could be lower than 800  $^\circ C.$ 

different oxidation degrees under different reacting conditions. These tests were performed and evaluated to select the most suitable oxygen carrier for gasification performance in a CLG unit. The following conclusions are drawn:

- The LD slag and iron sand have the highest gasification rate and gas yield among the four oxygen carriers under all the oxidation degrees and operational temperatures, which is relevant for their use in a CLG unit.
- ii) A higher oxidation degree of LD slag and iron sand can further improve the microalgae gasification rate but has a lower gas yield.
- iii) Behind the fast gasification, calcium in the LD slag and iron sand is seen playing a crucial role in catalytically enhancing the gasification and in absorbing the CO<sub>2</sub> and thus has higher concentrations of H<sub>2</sub> and CO in the gas product.
- iv) A route of calcium catalyst transfer to the char is proposed, and this explains the fast gasification with the LD slag and iron sand.
- v) LD slag and iron sand are selected for our next campaigns in a CLG pilot unit.

#### CRediT authorship contribution statement

**Daofeng Mei:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Francisco**  García-Labiano: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. Alberto Abad: Writing – review & editing, Supervision, Resources, Investigation, Conceptualization. Iñaki Adánez-Rubio: Writing – review & editing, Resources. Tobias Mattisson: Writing – review & editing, Supervision, Methodology, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2025.108266.

#### Data availability

Data will be made available on request.

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