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# Chemical looping combustion process in fixed-bed reactors using ilmenite as oxygen carrier: Conceptual design and operation strategy

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## HIGHLIGHTS

- The feasibility of fixed-bed CLC with methane and ilmenite as carrier is assessed.
- A conceptual design has determined operating windows for each stage of the system.
- Suitable recycles allow the advance of the fronts along the beds to be controlled.
- A steam reforming stage enhances the reduction of the carrier and the combustion efficiency.
- Results show technical viability of fixed-bed CLC and its potential for further development.

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## ABSTRACT

A process scheme based on fixed-bed reactors is presented as a possible alternative for carrying out the chemical looping combustion of methane at high pressure with ilmenite as oxygen carrier. The operation at high pressure permits the use of highly efficient power cycles. However, complex heat management strategies and switching valves able to function at very high temperatures are required. The continuous cyclic operation of a packed-bed chemical looping combustion process is described using a basic reactor model. A sequence of four stages: reduction, steam reforming, oxidation and heat removal ensures the production of a continuous high temperature and high pressure gas able to efficiently drive a gas turbine for power generation in combination with a steam cycle. At the same time, a concentrated stream of $CO_2$ suitable for transport and storage is also produced. The use of suitable recycles of product gases makes it possible to control the progression of the reaction and the heat exchange fronts, which improves the heat management of the CLC process. The inclusion of steam methane reforming in the process allows the conversion of the ingoing methane to syngas, which enhances the reduction kinetics of the ilmenite and the overall combustion efficiency of the process. A preliminary conceptual design for an inlet flow of 10 kg/s of methane (500 MWt) has shown that a minimum of five reactors, 10 m long, with an inner diameter of 6.7 m, would be required to fulfil the overall process assuming cycles of 10 min with maximum pressure drops per stage of less than 6%. These results demonstrate the potential of this novel technology for power generation in combination with $CO_2$ capture.

## 1. Introduction

The potential increase in world energy demand over the next few decades and the alarming signs of global warming make it necessary to drastically reduce greenhouse gas emissions from anthropogenic sources [1]. Of the different strategies directed at mitigating $CO_2$ emissions developed in recent years, carbon capture and storage (CCS) is considered as a valid mid-term solution [2]. $CO_2$ capture is nowadays the most energy-intensive step in CCS, and as a result, there is growing interest in the development of new $CO_2$ capture technologies, especially in large-scale power production in order to address the problem of energy penalties and the cost of existing equipment [3].

Of the different technologies proposed in the literature, chemical looping combustion (CLC) represents one of the most promising alternatives for achieving a very high $CO_2$ capture efficiency with reduced energy penalties [4]. This concept consists in the transfer of oxygen from air to the fuel by using a solid oxygen carrier (typically a metal oxide) and so avoiding any direct contact between the fuel and air. The dilution of the combustion products

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## Nomenclature

| | |
|---|---|
| $c_{pi}$ | specific heat capacity of component *i* (kJ/mol °C) |
| $\Delta H_r$ | enthalpy of the reaction (kJ/mol) |
| $M_i$ | molecular weight of component *i* (kg/mol) |
| $P$ | pressure (bar) |
| $t$ | time (s) |
| $T_{gin}$ | inlet gas temperature (°C) |
| $T_{max}$ | maximum temperature (°C) |
| $T_{s0}$ | initial temperature of bed reactor (°C) |
| $\Delta T_{max}$ | maximum adiabatic temperature variation (°C) |
| $u_e$ | heat exchange front velocity (m/s) |
| $u_g$ | gas velocity (m/s) |
| $u_r$ | reaction front velocity (m/s) |
| $x_i$ | weight fraction of component *i* (dimensionless) |

*Greek letters*

| | |
|---|---|
| $\rho_i$ | density of component *i* (kg/m$^3$) |
| $\varepsilon$ | porosity (dimensionless) |
| $\varphi$ | stoichiometric factor (dimensionless) |

with nitrogen is avoided and the resulting gas is highly concentrated in $CO_2$. CLC was firstly conceived in the 1950s [5], but it was not until the 1990s when it was proposed as a $CO_2$ capture system [6]. Most of the CLC configurations proposed consist of interconnected fluidized-bed reactors, where the oxygen carrier is reduced in the fuel reactor and rapidly transported to the air reactor to be regenerated [7–14]. The small size of the particles used in fluidized beds ensures that there is good contact between the gas and solids, as a result of which the kinetics of the reactions involved in the process are considerably enhanced. Furthermore, rapid mixing of the solids ensures an adequate control of the temperature, which is of fundamental importance in the energy-intense reactions characteristic of CLC processes. The application of the CLC concept in fluidized-beds has been widely studied in recent years in several experimental units at different pilot scales [13–20]. However, the use of interconnected fluidized-beds in CLC has several drawbacks. Operation at high pressure is required to enable a CLC system to be integrated in a combined cycle to increase the energy efficiency [21]. Several works have been published in recent years about CLC performed in fluidized-beds at high pressure [22–24], but this concept still faces critical challenges, such as the difficulty in maintaining a stable circulation of solids between the pressurized reactors, in order to demonstrate its feasibility on a large scale. Moreover, a high-temperature and high-pressure solids filtering system is required to eliminate the fines resulting from particle attrition, since the presence of particles in the exiting gas from the CLC unit could have a negative effect on the performance of the downstream gas turbine [4].

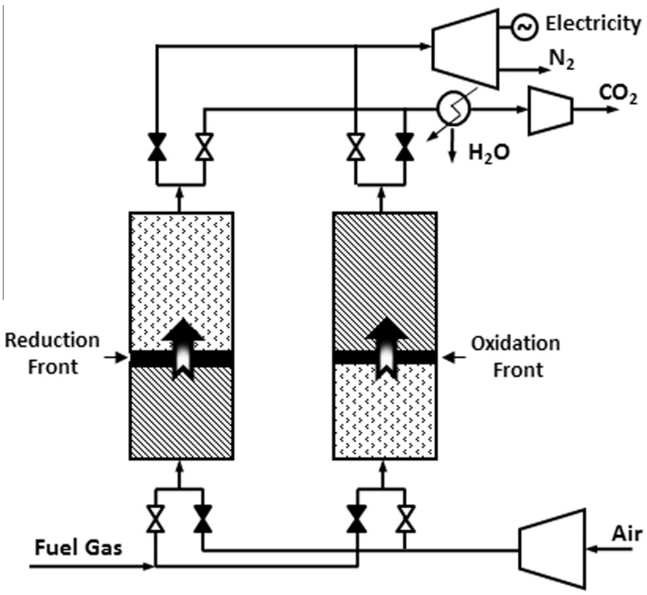

**Fig. 1.** Representation of a CLC system with alternating fixed-bed reactors for power generation.

An alternative for CLC applications at high pressure is the use of configurations based on dynamically operated fixed-bed reactors, where the oxygen carrier remains stationary and the gas feed (fuel gas and air, respectively) is periodically alternated in order to perform the reduction and oxidation stages. As can be seen from Fig. 1, the use of at least two reactors operating in parallel ensures: (1) the production of a continuous high-temperature and high-pressure stream of gas, that is able to drive a gas turbine for power generation, and (2) a concentrated stream of $CO_2$ suitable for transport and subsequent geological storage. In fixed-bed systems, attrition in the oxygen carriers can be expected to be negligible, and therefore, cyclones and filters downstream are not required. Moreover, the oxygen carrier can be better utilized, because operating in fixed-beds allows a larger degree of conversion between the reduced and oxidized forms. In contrast, heat management strategies for controlling the changes in temperature as the reaction fronts advance through the bed and switching valves able to function with gases at high temperature are required in fixed-bed systems. The high temperature valves required are one of the major drawbacks of this technology. There are commercial valves designed to operate at very high pressures and temperatures for over thousands of cycles, but further investigation is needed to improve their performance under the CLC operating conditions. Although there is a wide experience in industry with pressure and temperature swing adsorption systems, there are very few works that deal with the feasibility of CLC in fixed-bed configurations [25–28]. Early works on chemical looping processes carried out in fixed-beds [25] showed that the oxidation and reduction reactions involved can proceed very fast in narrow reaction fronts. During chemical looping combustion, both reaction and heat exchange fronts are formed and move forward at different velocities depending mainly on the concentration and molecular weights of the reactants and on the stoichiometry of the reactions [26], which is a similar phenomenon to the catalytic oxidation of a fuel gas when it is carried out at different operating temperatures [29]. Several heat management strategies have been proposed in the literature in relation with CLC for controlling the increase in temperature in the reaction fronts, while the product gas is discharged at nearly constant temperature and mass flow rate to protect the gas turbine from thermal and mechanical stress, and also to ensure that the temperature profiles of the solids are sufficiently high to allow fast reaction rates and total gas and solids conversion from the very beginning of the operation.

One option is to use an oxygen carrier with a sufficiently low content of active phase that allows the oxidation stage to be accomplished without exceeding the maximum allowable temperature (i.e. up to 1200 °C depending on the oxygen carrier in order