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# Operation of fixed-bed chemical looping combustion

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**Abstract**

Chemical Looping Combustion is an alternative technology for $CO_2$ capture. While most systems utilize dual circulating fluidized-beds, this work shows that fixed-bed Chemical Looping Combustion is a feasible configuration for this technology. The inherent separation of the $CO_2$ from the depleted air stream gives a very low efficiency penalty, which is further improved by the possibility of using a pressurized fixed-bed system, a factor much more difficult to realize with circulating fluidized beds. A laboratory scale experimental system has been constructed for the purpose of validating a numerical model. The results from the numerical model have agreed well with experimental data over full oxidation-reduction cycles and will be presented in subsequent publications. The work briefly described here, and to be presented in detail in coming publications, forms a basis which proves feasibility, but also opens up several possibilities for further investigations needed to scale-up and eventually commercialize CLC for power generation with inherent $CO_2$ capture.


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Keywords: Chemical Looping Combustion; $CO_2$ capture; fixed-bed; multiphase reactors

## 1. Introduction

Carbon capture and storage (CCS) has been demonstrated by the European Union to be a key area of innovation. Implementation of initiatives, such as the CCS Demonstration Project Network, show that it is crucial to realize widespread commercial applications of carbon-reduction technologies in order to meet the ambitious targets set forth by the Europe 2020 strategy. One of these technologies which has proven to be promising is Chemical Looping Combustion (CLC). It is a technology in which inherent $CO_2$ capture allows for the lowest theoretical efficiency penalty while also producing a stream of pure $CO_2$ and

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water, which can be easily stored underground or fed into a $CO_2$ conversion process, for example to make chemicals

The basis of CLC is that the combustion of a fuel is accomplished in two steps. First, the oxygen is taken up from air through the oxidation of a bed of metal particles, forming metal oxides and producing a stream of hot, depleted air. Second, the fuel is combusted as it flows through the metal oxide bed, reducing the bed back to metal and producing a stream of $CO_2$ and water. In this way, the metal particles, also called the oxygen carriers, are looped between oxidized and reduced states. This concept is most comparable with oxyfuel technologies, but the key advantage with CLC is the elimination of the need to first produce oxygen from air, usually requiring energy intensive cryogenic processes. With CLC, the separation of the $CO_2$ from air is inherent. Simple condensation of water from the reduction product stream yields essentially pure $CO_2$ that can be readily compressed for transport and storage.

## 2. CLC configurations

The conventional configuration for chemical looping systems is with dual circulating fluidized beds, as shown in Figure 1, which consists of a smaller reactor where the fuel is fed to reduce the metal oxides and a larger reactor where high volumes of air oxidize the metal. The very high volumes of flows needed for power generation are handled easily with large fluidized beds, which is a well-known technology from FCC and other processes. The ability to directly feed coal into the fluidized beds without prior gasification is another key advantage. However, some difficulties arise as the size of the particles and the gas flow rates must be chosen correctly so that the bed fluidizes, the particles have the optimal residence time in the reactor, and the fuel conversion is as high as possible. Sintering of the particles with the high operating temperatures, 900 – 1100 °C, is a major issue as the fluidization characteristics of the particles change and reactive surface area is lost. Operation at higher pressures (> 20 bar) and temperatures (>1100°C), which is desired for increased efficiency, makes this more difficult. Also, between the air and fuel reactors, the particles must be separated from the high flow of gases. This requires a large cyclone and seals that make the system more costly and increase the mechanical degradation of the particles. These factors become much more difficult to manage and introduce new technical difficulties with each new step up in scale.

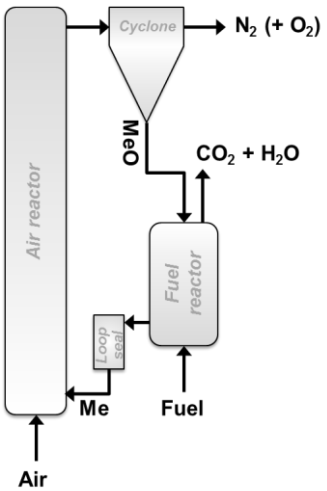


Fig. 1. Schematic of a dual circulating fluidized-bed CLC system

As an alternative to the circulating fluidized bed configuration, the authors of this paper have developed a fixed-bed CLC process that allows for much more flexibility in operating parameters and has no need for expensive cyclones and loop seals. [1, 2, 3] It has been noted that in a fixed-bed configuration, large valves will be needed and will be costly, but initial designs indicate that this will not be a showstopper. The concept, shown schematically in Figure 1, is to switch the feed gas to the reactor between air (for the oxidation step) and fuel (for the reduction step). For continuous flows, such as for the production of a hot stream of nitrogen to be sent to a gas turbine, at least two reactors would be operated simultaneously, one always being oxidized and another always being reduced. Scale-up is accomplished by first finding the optimal size for an individual reactor based on costs and operability, then simply adding more reactors running in parallel. The design is modular—no new technical hurdles are introduced with each consecutive step in scale and the time from development to demonstration is expected to be much shorter than with fluidized beds. Furthermore, the fixed-bed system will be much more easily pressurized, a key advantage when considering power generation applications with $CO_2$ capture.

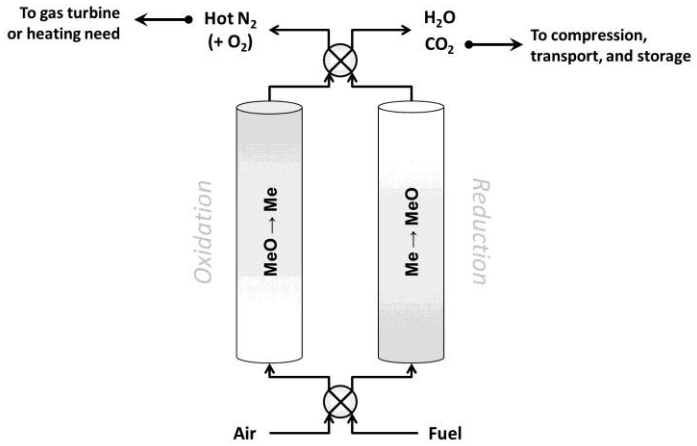


Fig. 2. Schematic of a fixed-bed chemical looping combustion system.

The topic of this work is the operation of a fixed-bed CLC system. This must be thoroughly understood before scale-up can be achieved optimally. A combined experimental and computational approach has been taken so that a validated numerical model can be used to predict how a system will operate over several cycles. Both the experimental setup and the model will be described with results shown for the model validation and further predictions. The influence of the operating conditions and cycle transitions on the potential to connect a fixed-bed CLC system with a gas turbine is also investigated.

## 3. Experimental setup

Several experimental systems have been developed ranging from tens of watts to 100 – 200 kW. While most of these are with CFB systems, fixed-bed CLC has also been demonstrated up to the 1 kW scale. Often, fixed-bed CLC has been considered to be infeasible due to sintering of the oxygen carrier particles leading to blockage of the flows and high pressure drops. However, Figure 3 shows that it is in fact possible to operate fixed-bed CLC without a significant rise in pressure. The data are from a 1 kW

reactor filled with copper-based particles as the oxygen carrier and contained within an oven set at 700°C. For the reduction step, shown on the left, syngas was used as a the fuel at a total flow rate of 2 L/min. In this particular experiment, the goal was to produce the maximum amount of pure $CO_2$ for subsequent reuse of the $CO_2$ (hence the low flow rates). The results show full conversion of the syngas for about 24 hours before the $H_2$ and CO start to break through. The pressure remains constant during this time at 0.16 bar over pressure. For the oxidation step, shown on the right, air was used with a flow rate of 6 L/min. The bed is oxidized fully, until the outlet concentration of $O_2$ is 20.5%, taking 36 hours to complete.

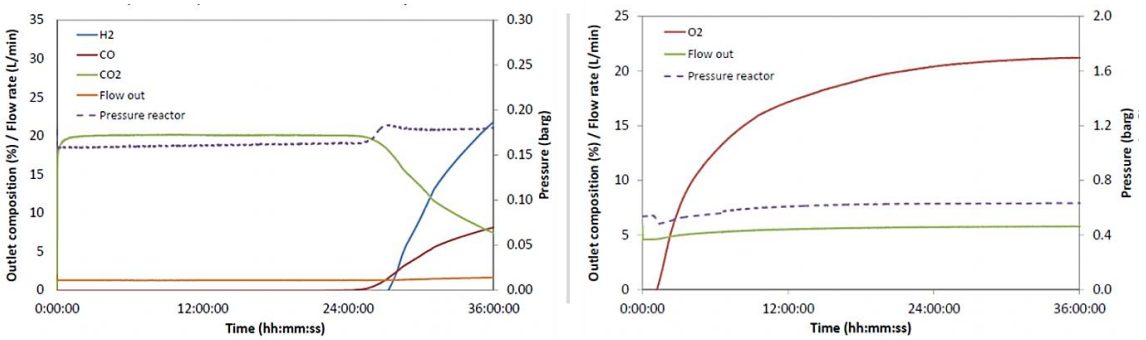


Fig. 3. Reduction (left) and oxidation (right) of a 1 kW fixed-bed CLC system with a copper-based oxygen carrier bed. The temperature was controlled at 700°C with total flow rates of 2 L/min syngas for the reduction and 6 L/min air for the oxidation.

While the 1 kW system shows the feasibility of operating fixed-bed CLC, a smaller 100 W system has been constructed at the Technical University of Eindhoven with modifications including 48 thermocouples along the length of the reactor, sections of inert material both before and after the bed, and the ability to be pressurized up to 3 bar. The purpose of this smaller setup is to allow for the validation of a numerical model developed in the same group. The many thermocouples allow for validation of the axial temperature profiles while gas analysis data validates the outlet concentrations of the gases. The details of the experimental setup and results will be given in an article to be published shortly by the same authors.

## 4. Numerical model

The numerical model mentioned above has been described thoroughly elsewhere; it will be described briefly here, but for more details, the reader is referred to the papers of S. Noorman [1, 2]. The model was developed in order to investigate the dynamic behavior of the process over multiple oxidation/reduction cycles. It is based on a 1D adiabatic packed bed reactor model with the important assumptions that (i) there are no radial temperature or concentration gradients, (ii) heat transfer limitations from the gas phase to the solid phase can be accounted for in the effective heat dispersion (pseudo-homogeneous model), and (iii) heat losses through the reactor wall can be accounted for by a constant heat transfer coefficient (45 W $m^{-2}$ $K^{-1}$). The influence of axial dispersion, reaction kinetics, and changing physical properties of the gas and solid components involved have been incorporated and the effects of the pressure drop and change in the mass flow due to the gas/solid reactions are fully accounted for.

Copper oxide on alumina was selected as a model oxygen carrier. This system may not be considered as the most suitable oxygen carrier for this process, considering its low melting temperature and low oxidation cycle efficiency, but the availability of kinetic data for both the oxidation and the reduction

reactions [3] make this system well suited for introductory calculations. The choice of the oxygen carrier is not expected to affect conclusions drawn from modeling studies in a qualitative sense. The results from the simulations, both in comparison with experimental data for validation and from investigations into larger scales and different configurations, will be presented in an article soon to be published by the same authors.

## 5. Summary

The results presented here show that fixed-bed Chemical Looping Combustion is a feasible configuration for this technology, which shows strong promise for power generation with $CO_2$ capture. The inherent separation of the $CO_2$ from the depleted air stream gives a very low efficiency penalty, which is further improved by the possibility of using a pressurized fixed-bed system, a factor much more difficult to realize with circulating fluidized beds.

A laboratory scale experimental system has been constructed for the purpose of validating a numerical model. The results from the numerical model described here have agreed well with experimental data over full oxidation-reduction cycles and will be presented in subsequent publications. Simulations of operation at larger scales and with varying configurations will be discussed.

Overall, fixed-bed CLC is a promising technology. The work briefly described and to be presented in detail in coming publications forms a basis which proves feasibility, but also opens up several possibilities for further investigations needed to scale-up and eventually commercialize CLC for power generation with inherent $CO_2$ capture.

## Acknowledgements

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