Chemical Engineering Journal 310 (2017) 226–239

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# *In situ* gasification Chemical-Looping Combustion of coal using limestone as oxygen carrier precursor and sulphur sorbent

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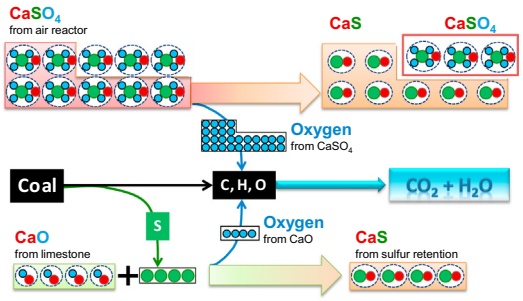
## HIGHLIGHTS

- The novel Limestone Chemical Looping Combustion (LCL-C™) process is investigated.
- Process allows the coal combustion with $CO_2$ capture and in-situ desulphurisation.
- No drawback referred to thermal integration has been detected.
- TGA tests determined that sulphated limestone is a feasible oxygen carrier.
- Sulphated limestone exhibited a high oxygen transport capacity, ≈16.7 wt.%.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 29 August 2016
Received in revised form 24 October 2016
Accepted 25 October 2016
Available online 26 October 2016

*Keywords:*
$CO_2$ capture
Chemical Looping Combustion
Coal
Desulphurization
Calcium-based sorbent
Oxygen carrier

## ABSTRACT

In-situ Gasification Chemical-Looping Combustion (iG-CLC) burning coal is achieving a great interest due to the possibility of using low cost oxygen carriers such as $CaSO_4$. The Limestone Chemical Looping Combustion process (LCL-C™) registered by Alstom Power Inc. proposes the use of a continuous $CaCO_3$ feeding together with coal to produce $CaSO_4$ as an oxygen carrier via sulphur retention. The operation is similar to what happens in a circulating fluidized bed boiler burning coal. In the present research work, the study of thermodynamic equilibrium limitations together with mass and enthalpy balances have been carried out for a CLC system in order to investigate whether the LCL-C™ process is a promising and energy efficient option to carry out the coal combustion with $CO_2$ capture and in-situ desulphurisation. So, no limitations were found to transfer the required oxygen from air to fuel using sulphated limestone as oxygen carrier for whatever coal used. The selection of a suitable oxygen carrier to fuel ratio mainly depends on the sulphur content of the coal used. In addition, no drawback referred to thermal integration in the system has been detected. Thus, operation at 950 °C in the fuel reactor to avoid $SO_2$ release via side reactions, and 1050 °C in the air reactor is feasible. Likewise, experimental tests have been performed in a thermogravimetric analyser to evaluate the capability of a limestone to be sulphated and to transfer oxygen. A value of the oxygen transport capacity of about 16.7 wt.% was obtained. This value is four times higher than that of others typical inexpensive oxygen carriers published in literature.



## 1. Introduction

Nowadays, it is globally recognized that the release of greenhouse gases, and especially $CO_2$, into the atmosphere from fossil fuel combustion in power plants is the mainly responsible for the so-called Global Warming. Recently, the 21st United Nations

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http://dx.doi.org/10.1016/j.cej.2016.10.113
1385-8947/

Climate Change Conference (COP21) [1] was celebrated in Paris where representatives of 195 countries were present in order to slow down the increase of atmospheric $CO_2$ in the future. The main agreement reached was to maintain the increase of global temperature below 2 °C with respect to pre-industrial period, that is, not to reach $CO_2$ concentration in the atmosphere higher than 450 vppm. Several options are needed to minimize $CO_2$ emissions in a short-medium term such as reducing energy consumption, using renewable sources, fossil fuels with low carbon content, nuclear energy as well as $CO_2$ capture and storage (CCS) technologies [2].

In this context, Chemical Looping Combustion (CLC) is a promising technology to carry out the $CO_2$ capture at low economic and energetic cost. CLC is based on the transfer of the oxygen from air to the fuel by means of a solid oxygen carrier to avoid the direct contact between them. The majority of the CLC plants use the configuration composed of two interconnected fluidized bed reactors, fuel and air reactors, with a particulate oxygen carrier circulating between them [3].

The CLC technology to burn solid fuels like coal is achieving a high degree of development [3,4] since it is expected that they continue being one of the main energy sources in a medium term [5]. Among the different approaches to perform the combustion of solid fuels in CLC systems, the *in-situ* Gasification CLC (*i*G-CLC) is focusing great attention because of the possibility of using low cost oxygen carriers [6]. In *i*G-CLC, the solid fuel is introduced and mixed with the oxygen carrier in the fuel reactor where it is directly gasified by steam and/or $CO_2$; see Fig. 1. Then, coal gasification products are burnt by the oxygen carrier via a gas-solid reaction. Once the oxygen carrier is reduced in the fuel reactor, it is transported to the air reactor to be oxidized in order to start a new redox cycle. The net chemical reaction as well as the heat involved in the global process is the same as for usual combustion.

In *i*G-CLC, the $CO_2$ capture efficiency greatly depends on the char gasification rate which is the limiting step. To maximize the char conversion in the fuel reactor, thus increasing the $CO_2$ capture, high reactor temperature and the use of a highly reactive oxygen carrier are advised to increase the char gasification rate [7]. But the use of a highly efficient carbon separation system, e.g. a carbon stripper, is required in order to reach $CO_2$ capture rates close to 100%; see Fig. 1 [8]. Thus, $CO_2$ capture efficiency values close to 100% were reached in a 100 $kW_{th}$ CLC unit [9] by using a highly efficient carbon stripper [10].

A critical aspect in deploying the CLC technology is to select an appropriate oxygen carrier. In the case of CLC with solids, the cost of the oxygen carrier and its environmental friendly behaviour are very relevant characteristics since it is inevitable that some oxygen carrier particles are extracted with the coal ashes when they are removed from the system. Therefore, the use of natural ores or by-products from industrial processes, which are inexpensive and widely available, could be a promising option to develop *i*G-CLC technology. Up to now, most of the studies have been focused on iron-based materials from different origins such as ilmenite, which has been intensively used in pilot units from 0.5 $kW_{th}$ to 1 $MW_{th}$ burning coal [9,11–15]. In these cases, complete combustion was not achieved, and unconverted products such as $H_2$, CO and $CH_4$ are present in the $CO_2$ stream exiting the fuel reactor, which can be addressed by means of an oxygen polishing step. Combustion efficiency has been improved by using more reactive materials, e.g. iron and manganese ores or waste Fe-enriched sand fraction from alumina production, but complete combustion was still not reached [16–18]. In addition, several design improvement have been evaluated in order to enhance the combustion efficiency [19].

Besides, the use of materials with the capability to release gaseous oxygen in the fuel reactor have been proposed to improve the *i*G-CLC performance, in the so-called Chemical Looping with Oxygen Uncoupling (CLOU) [20]. Thus, synthetic materials based on copper oxide, have shown excellent performance regarding combustion efficiency [21] whereas the oxygen uncoupling capability of Mn-Fe and Ca-Mn materials improved the combustion efficiency of coal and wood char [18,22].

In addition to these materials, sulphated limestone has been used as oxygen carrier in a 3 $MW_{th}$ CLC unit by Alstom in the so-called Limestone Chemical Looping Combustion process, LCL-C™ [23]. In the LCL-C™ process either $CaSO_4$ formed *in-situ* by the limestone reaction with sulphur from coal or $CaSO_4$ present in ash from coal combustion in a circulating fluidized bed (CFB) is proposed as an oxygen carrier material. Nevertheless, with the exception of the fact that a good performance regarding $CO_2$ capture was achieved [24], there is no detailed information available in literature regarding the LCL™ process. These excellent results would be attributed to the use of a novel oxygen carrier (sulphated limestone) and/or the conceptual design of the 3 $MW_{th}$ CLC unit. New advances and future perspectives have been recently reported [25].

The main chemical reactions involved in the *i*G-CLC process using $CaSO_4$ as oxygen carrier are compiled in Table 1. Desired reactions in the fuel reactor are referred to combustion of CO, $H_2$ and $CH_4$ (R1–R3).

The advantages in the use of $CaSO_4$ as an oxygen carrier are its broad availability, low cost and high oxygen transport capacity. The oxygen transport capacity of $CaSO_4$ is 47 wt.% which is consid-

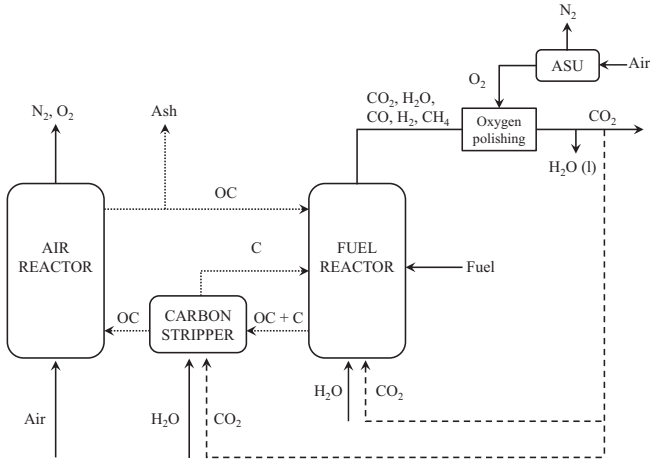


**Fig. 1.** General scheme of iG-CLC process.

**Table 1**
Chemical reactions involved in iG-CLC using $CaSO_4$ as oxygen carrier.

| | | |
|---|---|---|
| CLC related chemical reactions | | |
| FR | $CaSO_4 + 4\ CO \rightarrow CaS + 4\ CO_2$ | (R1) |
| | $CaSO_4 + 4\ H_2 \rightarrow CaS + 4\ H_2O$ | (R2) |
| | $CaSO_4 + CH_4 \rightarrow CaS + CO_2 + 2\ H_2O$ | (R3) |
| | $CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2$ | (R4) |
| | $CaSO_4 + H_2 \rightarrow CaO + SO_2 + H_2O$ | (R5) |
| | $4\ CaSO_4 + CH_4 \rightarrow 4\ CaO + 4\ SO_2 + CO_2 + 2\ H_2O$ | (R6) |
| | $3\ CaSO_4 + CaS \rightarrow 4\ CaO + 4\ SO_2$ | (R7) |
| | $CaSO_4 \rightarrow CaO + SO_2 + 1/2\ O_2$ | (R8) |
| AR | $CaS + 2\ O_2 \rightarrow CaSO_4$ | (R9) |
| | $CaS + 3/2\ O_2 \rightarrow CaO + SO_2$ | (R10) |
| Reactions involving limestone and sulphur in coal | | |
| | $CaCO_3 \rightarrow CaO + CO_2$ | (R11) |
| | $CaO + H_2S \rightarrow CaS + H_2O$ | (R12) |
| | $CaSO_4 + 4/3\ H_2S \rightarrow CaS + 4/3\ SO_2 + 4/3\ H_2O$ | (R13) |
| | $CaO + SO_2 \rightarrow CaSO_3$ | (R14) |
| | $CaSO_3 + CO_2 \rightarrow CaSO_4 + CO$ | (R15) |
| | $CaSO_3 + H_2O \rightarrow CaSO_4 + H_2$ | (R16) |