Fuel Processing Technology 171 (2018) 78–88

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Relevance of plant design on CLC process performance using a Cu-based oxygen carrier

Alberto Abad*, Pilar Gayán, Francisco García-Labiano, Luis F. de Diego, Juan Adánez

Dept. of Energy and Environment, Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, Zaragoza 50018, Spain

ARTICLE INFO

Keywords:
CO_2 capture
Chemical Looping Combustion
Copper
Methane
Modelling
Fluidized bed

ABSTRACT

Previously validated mathematical CLC models were used to simulate the process performance of CLC methane combustion using an impregnated Cu-based material and to analyse the effect of the fuel reactor design; being either a bubbling fluidized bed or a circulating fluidized bed. The CLC models considered both the fluid dynamic of the fluidized beds at the specific regime and the corresponding kinetics of oxygen carrier reduction. From the model outputs, the performance of the different systems was assessed by calculating the methane conversion in the fuel reactor. Main results highlights that the selection of a suitable particle size of the oxygen carrier and cross section area are key factors to achieve complete combustion with low solids inventory in the fuel reactor. In addition, the growing of bubbles should be limited in order to achieve high CH_4 conversion with low solids inventory values, mainly in the bubbling regime with low cross section areas. Complete combustion was predicted with solids inventory in the fuel reactor of 250 kg/MW_{th} (1 m^2/MW and particle size of 0.25 mm) or 125 kg/MW_{th} (0.2 m^2/MW and a particle size of 0.15 mm) in the bubbling and turbulent regime, respectively. Considering the pressure drop related to these conditions, conclusions for the optimization design of a CLC unit using the Cu-based oxygen carrier are drawn based on the results of the modelling and simulation.

1. Introduction

Chemical Looping Combustion, CLC, is one of the most promising processes to capture CO_2 with low economic, energetic and environmental costs [1]. CLC is based on the transfer of the oxygen from air to the fuel by using a solid oxygen carrier. One of the most used configurations for CLC units is the use of two interconnected fluidized bed reactors, with the oxygen carrier material circulating between them; see Fig. 1. In the fuel reactor, the oxygen carrier is reduced while the fuel is oxidized. In the air reactor, the oxygen carrier is oxidized again with air to its original state. The net chemical reaction and combustion enthalpy is the same as in a conventional combustion, where the fuel is burned in direct contact with oxygen from air. It is highlighted that the CO_2 capture is inherent to the CLC process, as the air is not mixed with the fuel.

CLC technology for gaseous fuels has been successfully demonstrated with > 4000 h of operational experience in continuous CLC plants up to 150 kW_{th} using > 40 different oxygen carriers [2]. Among them, a Cu-based material has been developed and selected as a promising material for the scale-up of the process [3]. This material was prepared by the impregnation method, which is adequate for production of large amounts of particles at low cost. Our research group at Instituto de Carboquímica (ICB-CSIC) has optimized the impregnation method to develop highly reactive Cu-based materials without tendency towards agglomeration of particles during the operation in a fluidized bed [4]. This material is able to properly burn gaseous fuels such as syngas and CH_4, even with some fractions of impurities such as light hydrocarbon or H_2S [5–7]. In addition, evaluation of the operating conditions and selection of the alumina support has been performed with the target of improve the life-time of particles [8,9], which eventually has been estimated to be up to 5000 h for an optimized material [3]. A maximum temperature in the fuel reactor about 800–850 °C is highly recommended, while the avoidance of $CuAl_2O_4$ formation can improve the durability of the particles.

Impregnated Cu-based oxygen carriers have been tested in several CLC facilities with promising results. These units can be classified depending on the fluid dynamic characteristics of the fuel reactor. Thus, 10 kW_{th} CLC units located at ICB-CSIC [10,11] and IFP [12] were designed for bubbling fluidized bed conditions in the fuel reactor, while the fuel reactor in the 120 kW_{th} unit and TUV [13–15] and 150 kW_{th} unit at SINTEF [16] were circulating fluidized beds. Recently, the 120 kW_{th} CLC unit at TUV has been modified to include a wider section in the bottom part of the reactor, but maintaining the circulation of solids in a narrow riser above the bottom bed [17]. Fig. 2 shows

* Corresponding author.
E-mail address: abad@icb.csic.es (A. Abad).

https://doi.org/10.1016/j.fuproc.2017.09.015
Received 23 June 2017; Received in revised form 5 September 2017; Accepted 19 September 2017
0378-3820/

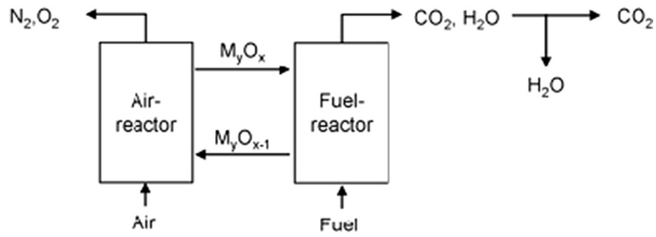


Fig. 1. Reactor scheme of the CLC process.

schemes of all these units where impregnated Cu-based oxygen carriers developed by ICB-CSIC have been tested.

When the fuel reactor was a bubbling fluidized bed reactor, complete combustion was achieved during operation in CLC units when the oxygen carrier to fuel ratio value was above $\phi = 1.5$ [6–11] whatever the particle size used in the 100–500 μm interval, and even with solids inventory values in the fuel reactor as low as 350 kg/MW$_{th}$. However, complete combustion was not achieved with these particles in circulating fluidized bed conditions, when maximum CH_4 conversion values of 70–80% with solids inventory values in the 200–400 kg/MW$_{th}$ interval [14]. But near complete CH_4 conversion has been achieved with 120 kg/MW$_{th}$ in the fuel reactor when the particle size of impregnated materials was limited below 200 μm [16]. These results suggest that factors affecting to the fluid dynamic of the fuel reactor, such as gas velocity and particle size can affect to the performance of the oxygen carrier in a CLC unit.

The next challenge is to upscale the CLC technology from 150 kW$_{th}$ to 10 MW$_{th}$ since there is a promising niche application in on-field steam generation with carbon dioxide capture and storage (CCS). Successful upscaling of this technology is highly dependent on two key aspects, namely 1) upscaling of reactor system and 2) upscaling of oxygen carrier manufacture. Most efforts are being allocated to upscale the CLC system designs to the desired power of 10 MW$_{th}$ [18]. Considering the results obtained in CLC plants above described, careful design of the fuel reactor must be considered to achieve the desired complete combustion of natural gas. In this sense, modelling is a relevant tool before the design, optimization and scale-up of the CLC process.

In this work, two theoretical models are used to analyse the relevance of the fuel reactor design on the performance of an impregnated Cu-based oxygen carrier burning methane in CLC. In this way, a CLC model for the fuel reactor in the 10 kW$_{th}$ CLC unit at ICB-CSIC was developed for a bubbling fluidized bed. The second fuel reactor model was developed to simulate the 120 kW$_{th}$ unit at TUV, where the fuel reactor was a circulating fluidized bed. Simulations of these CLC units allowed obtaining optimized conditions depending on the regime flow. From the results obtained, a brief discussion is included where relevant suggestions are drawn for a safe scale-up of the CLC process.

2. Mathematical models

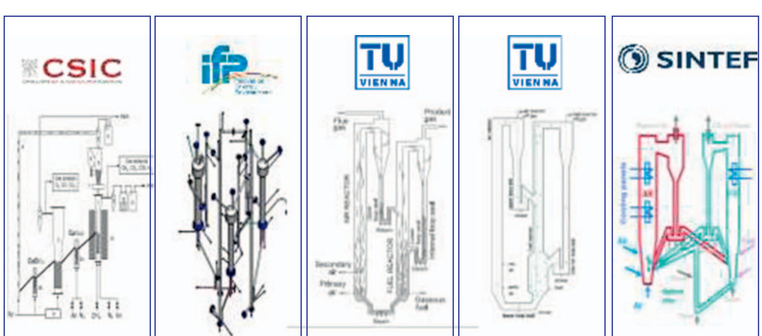
Dedicated theoretical models for the fuel reactor were developed in Fortran Code® considering the geometry and operating conditions existing in both the 10 kW$_{th}$ CLC unit at ICB-CSIC [10] and 120 kW$_{th}$ CLC unit at TUV [14]. The bubbling fluidized bed model was validated for the Cu-based material [19], while the model in turbulent regime was validated using Ni-, Fe,- Cu- or Mn-based materials as oxygen carrier [20–22], as well as ilmenite with solid fuels [23].

The models included the main processes affecting to the reaction of fuel gas with the oxygen carrier, such as reactor fluid dynamics, reactivity of the oxygen carrier and mechanism of the reaction. The reaction mechanism and reactivity depends on the pair gas-oxygen carrier considered, whereas the fluid dynamics is linked to the design and operating conditions of the reactor. Thus, the models were composed of two modules, the fluid dynamic and the mass balances to reacting compounds, which must be solved simultaneously due to the gas expansion of CH_4 when it is converted to CO_2 and H_2O. The oxygen carrier considered was the impregnated Cu-based oxygen carrier tested in both CLC units.

2.1. Fluid dynamics

The fluid dynamic properties of the fuel reactors affect not only to the solids distribution in the reactor, but also to the mass transference processes. Considering the impregnated oxygen carrier burning methane, the fluidization regime flow will depend on the gas velocity and the particle size of solids; see Fig. 3. Thus, low gas velocity was used in the 10 kW$_{th}$ CLC unit to be operated in the bubbling regime. On the contrary, a higher velocity was used in the 120 kW$_{th}$ CLC unit, which implies the fuel reactor was operated in the turbulent regime. It is interesting to note that the gas volume is increased up to a factor of 3 during CH_4 conversion to CO_2 and H_2O, and the gas velocity inside the fuel reactor was correspondingly increased.

The fluid dynamic model was adapted to the specific characteristics of every unit. The main equations involved in the fluid dynamic models are gathered in Table 1. More information about the specific details on the model for bubbling or turbulent regime can be found elsewhere [19,28]. Note that in some cases the same equation is valid for bubbling and turbulent regime due that both models are based on the two-phase flow theory by Kunii and Levenspiel [25], as it was adapted by



	ICB-CSIC	IFP - TOTAL	TUV	TUV	SINTEF
COUNTRY	SPAIN	FRANCE	AUSTRIA	AUSTRIA	NORWAY
Power (kW$_{th}$)	10	10	120	120	150
Configuration	BFB-BFB	BFB-BFB-BFB	CFB-CFB	CFB-CFB	CFB-CFB
Operat. time (h)	200	160	100	25	n.a.

Fig. 2. Schemes of the CLC units where impregnated Cu-based oxygen carrier materials developed by ICB-CSIC have been tested [10–17]. BFB: bubbling fluidized bed; CFB: circulating fluidized bed.