Full Length Article

# Dynamic simulation of fluidized bed chemical looping combustion process with iron based oxygen carrier

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## ARTICLE INFO

## ABSTRACT

Chemical looping combustion is a promising energy conversion technology for fossil fuel combustion with inherent carbon dioxide separation and minimum energy losses. A full understanding of the dynamic behavior is of paramount importance to successfully implement this technology at commercial scale. In this work, a dynamic mathematical model has been developed to simulate interconnected fluidized bed reactors of a 1 $MW_{th}$ syngas-based chemical looping combustion process with iron based oxygen carrier. The model consists of mass and energy balances equations as well as the equations that describe the hydrodynamics and heat transfer processes. The particles distribution inside the fluidized bed reactors is described by a 1.5-D hydrodynamic model. The model showed two zones in axial direction (an upper lean zone and a bottom dense zone) and a horizontal separation between core region and wall layer. Different heat transfer mechanisms have been taken into account: convection between gas phase and the oxygen carrier particles; convection of the moving particle phase with wall and radiation. The developed model was used to predict (in space and time): gas and solid velocity distribution, gas composition distribution, behavior of oxygen carrier, and temperature profiles inside the air and fuel reactor. The dynamic behavior of the chemical looping combustion process was studied by step and ramp input changes in the input gas flow rate.

## 1. Introduction

Towards a better understanding of the world's climate and of the long-term impact of climate change, significant progress has been made in the last decades. The Intergovernmental Panel on Climate Change (IPCC) [1] showed that "most of the observed increase in globally averaged temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations". $H_2O$, $CO_2$, $CH_4$, $N_2O$, CFCs and $SF_6$ are the main gases that contribute to global warming and $CO_2$ is the most prevalent of greenhouse gases. The main sectors that contribute the most to global greenhouse gas emissions are: heat & power, industry, building, transport, agriculture, forestry and waste management. The energy sector causes the most of greenhouse gas emissions (in Europe, fuel combustion and fugitive emissions from fuels represented 55% of the greenhouse gas emissions, in 2014). Several options are investigated for mitigating $CO_2$ from the energy sector: renewables, nuclear, low carbon content fuel, increasing the efficiency of the fuel conversion and $CO_2$ capture and storage.

The renewable energy sources (e.g. biomass, solar, wind) due to their higher cost, are not yet competitive with fossil fuels in current market conditions. Nuclear energy faces barriers such as uncertainty regarding long term waste management, safety issues and adverse public opinion. Hence, fossil fuels will remain the major energy resource for the next decades and the use of coal will increase according to projections from the International Environmental Agency (IEA). Carbon Capture and Storage (CCS) seems to be a very promising method to significantly decrease $CO_2$ emissions from coal fired power plants. Different carbon dioxide capture techniques are currently investigated: pre-combustion, in which the fuel is decarbonized prior to combustion; oxy-fuel combustion, which uses nearly pure oxygen and post-combustion, which separate $CO_2$ form the flue gases using different approaches. All these carbon-capture techniques are energy intensive, resulting in increased fuel needs for coal fired power plants by 25–40%, and an increase of the energy production by 21–91% [2]. Considering all these factors a new technology, Chemical Looping Combustion (CLC), was proposed to increase thermal efficiency in power plants. CLC has the potential to be one of the most efficient and low cost technologies, with inherent advantages for $CO_2$ separation [3].

Chemical looping combustion involves the use of a metal oxide as an oxygen carrier (OC). The oxygen carrier makes a closed cycle between two interconnected reactors: in the fuel reactor the fossil fuel

## Nomenclature

| | | | |
|---|---|---|---|
| $A_0$ | area of distributor plate per orifice, m$^2$/orifice | | phase, % |
| $A_B$ | cross sectional area of bed, m$^2$ | $e$ | emissivity, - |
| $A_p$ | heat transfer area of bed, m$^2$ | $f$ | function, - |
| $C_g$ | reactive gas concentration, mol/m$^3$ | $g$ | gravitational acceleration constant, m/s$^2$ |
| $F_j$ | gas/solid mass flow, kg/s | $k$ | thermal conductivity, - |
| $G_s$ | solid circulation rate, kg/(m$^2$·s) | $m$ | mass load, kg |
| $G_s^*$ | saturated flux of solids out of reactor, kg/(m$^2$·s) | $z$ | height of vertical position in the reactor, m |
| $H_{dz}$ | dense zone height, m | | |
| $H_{pg}$ | particle-gas heat flux, kJ/m$^3$·s | | |

*Greek letters*

| | |
|---|---|
| $\alpha$ | stoechiometric coefficient of components, - |
| $\beta$ | stoechiometric coefficient of solid components, - |
| $\delta_b$ | volumetric fraction of bubbles, - |
| $\delta_w$ | thickness of annulus zone, m |
| $\varepsilon_b$ | average bed porosity at a fixed position in the bottom bed, - |
| $\varepsilon_{dz}$ | dense zone voidage, - |
| $\varepsilon_e$ | emulsion voidage, - |
| $\varepsilon_{mf}$ | porosity at minimum fluidization conditions, - |
| $\varepsilon_{s,dz}$ | solid fraction/concentration in the dense zone, - |
| $\varepsilon_s$ | solid fraction/concentration in the reactor, - |
| $\varepsilon_s^*$ | saturation carrying capacity of gas, - |
| $\rho_g$ | gas density, kg/m$^3$ |
| $\rho_p$ | particle density, kg/m$^3$ |
| $\mu$ | gas viscosity, Pa·s |
| $\sigma$ | Stefan-Boltzmann constant = $5.6703e-8$, W/m$^2$ K$^4$ |
| $\tau$ | reaction time, s |
| $\psi$ | ratio of the visible bubble flow to the total flow through the bubbles, - |
| $\phi$ | sphericity - |

Nomenclature continued (left column):

| | |
|---|---|
| $H_{pw}$ | particle-wall heat flux, kJ/m$^3$·s |
| $H_r$ | heat of reaction, kJ/m$^3$·s |
| $N_t$ | number of orifices in the distributor, - |
| $Re_{mf}$ | minimum fluidization Reynolds number, - |
| $U_0$ | superficial gas velocity, m/s |
| $U_{br}$ | bubble riser velocity, m/s |
| $U_g$ | total gas flow, m/s |
| $U_{mf}$ | minimum fluidization velocity, m/s |
| $U_t$ | terminal velocity, m/s |
| $U_{tf}$ | gas throughout flow, m/s |
| $U_v$ | visible bubble flow, m/s |
| $X_{OC}$ | oxygen carrier conversion, - |
| $a_d$ | decay factor, 1/m |
| $d_b$ | bubble diameter, m |
| $d_{b0}$ | initial bubble size, m |
| $d_{bm}$ | maximum bubble diameter, m |
| $d_p$ | particle diameter, m |
| $k_S$ | kinetic constant, 1/s |
| $x_i$ | component fraction, - |
| $\Delta P$ | pressure drop, kPa |
| $h$ | height above the bottom of the bed, m |
| $h_{pg}$ | particle-gas heat transfer coefficient, kW/m$^2$·K |
| $h_{pw}$ | particle-wall heat transfer coefficient, kW/m$^2$·K |
| $h_r$ | radiative heat transfer coefficient, kW/m$^2$·K |
| $A$ | cross sectional area of bed/reactor, m$^2$ |
| $Ar$ | archimedes number, - |
| $Cp$ | specific heat, kJ/kg·K |
| $M$ | molecular mass, g/mol |
| $Pr$ | Prandtl number: $Pr = Cp \cdot \mu/k$, - |
| $R$ | ideal gas constant = 8.314, J/mol·K |
| $S$ | heterogeneous reaction source term, kg/s·m |
| $T$ | Temperature, K |
| | volumetric concentration of bed particles in the dispersed |

*Subscripts*

| | |
|---|---|
| $dz$ | dense zone |
| $g$ | gas |
| $i$ | component |
| $p$ | particle |
| $s$ | solid |
| $tz$ | transport zone |
| $w$ | wall |
| $c$ | cluster |
| $l$ | lean particle phase |

combustion takes place using the lattice oxygen of the metal oxide and in the air reactor the oxygen carrier is regenerated by oxygen from air. Therefore, CLC technology avoids direct contact between fuel and air and presents inherent sequestration of $CO_2$ without additional energy consumption. Complete combustion in the fuel reactor produces only $CO_2$ and water vapor. The outlet gas stream of the air reactor contains nitrogen and unreacted oxygen.

The overall reaction in the fuel reactor is the following:

$$(2n + m)M_yO_x + C_nH_{2m} \rightarrow (2n + m)M_yO_{x-1} + mH_2O + nCO_2$$
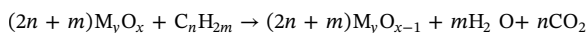
The OC is reoxidized, in the air reactor, according to the following reaction:

$$M_yO_{x-1} + 1/2O_2 \rightarrow M_yO_x + (N_2 + \text{unreacted} O_2)$$
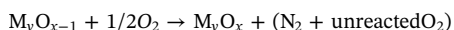
In order to be used in a CLC process, the oxygen carrier should meet the following criteria: to be environmentally friendly, to have satisfactory thermodynamic properties for fuel conversion, to have high reactivity in both process steps (oxidation and reduction), low attrition as to be used in reasonable number of cycles, to have high melting points, low agglomeration tendency, mechanical strength in order to be able to be processed at desired particle size and to be economically feasible. Different types of oxygen carriers (e.g. Ni, Cu, Fe, Mn, Co-based oxides) should fulfill the above desired characteristics. Pure metal oxides, metal oxides mixed with supports (e.g. $Al_2O_3$, $SiO_2$, $TiO_2$, or $ZrO_2$) or combinations of metal oxides have been tested to get the desired properties [2,4]. The Fe-based oxygen carriers are suitable for chemical looping combustion applications because they are environmentally friendly, non-toxic for nature, less susceptible to carbon formation and have a good reactivity. Since iron ores occur naturally (such as magnetite, hematite, ilmenite, limonite, etc.), Fe-based oxygen carriers are inexpensive. The oxygen carrier used in this work is activated ilmenite. According to literature, ilmenite's reactivity increases after a number of 5–20 redox cycles, after which the reactivity remains mostly constant, so the activation process is relatively fast and can be done inside the chemical looping process [5].

The chemical looping process can be used either with gas, liquid or solid fuel, in the combustion step. In CLC of gaseous fuels, the oxygen carrier reacts directly with the primary fuel (e.g. natural gas, refinery