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Prompt considerations on the design of Chemical-Looping Combustion of coal from experimental tests

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ABSTRACT

The Chemical-Looping Combustion of coal in the reactor system has been proposed as an interesting option to process a solid fuel in a CLC system. In this process, a solid fuel is directly fed to the fuel reactor in a CLC system. Solid fuel pyrolysis, char gasification and oxidation of gaseous products by reaction with the oxygen-carrier are the main chemical processes happening in the fuel reactor. The aim of this study is to analyze the performance of ilmenite as oxygen-carrier for CLC of coal regarding to the conversion of gaseous products from char gasification. Successive reduction–oxidation cycles were carried out in a fluidized bed using bituminous coal char as reducing agent. The changes on chemical and physical properties of ilmenite particles were determined. An activation process of ilmenite through the redox cycles was evidenced which was justified by an increase of porosity. The results showed that the activation for ilmenite reduction reaction was completed after seven redox cycles. However, the oxidation reaction rate was increasing still after 16 redox cycles because the porosity was not fully developed. The gasification reaction rate and the ilmenite reactivity were analyzed. The effect of ilmenite itself and the influence of the gasification agent, i.e. H_2O, CO_2 or H_2O/CO_2 mixtures, and temperature on the gasification rate were evaluated. Limited use of CO_2 in the fluidizing gas was identified in order to maintain high gasification rates. Higher temperature improved the char gasification rate, mainly using steam as gasification agent, and the combustion efficiency of the gasification products. Nevertheless, the effect of temperature on the combustion efficiency was of lower relevance than that on the gasification rate. Finally, a theoretical approach was developed to easily evaluate the conversion of char in the fuel-reactor by gasification.

1. Introduction

According to the Intergovernmental Panel on Climate Change (IPCC) [1], “most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations”. There is therefore a broad acceptance by scientists of the link between greenhouse-gas emissions and global climate change. As the use of fossil fuels in energy generation represents about 65% of global anthropogenic greenhouse-gas emissions [2], actions geared to reduce emissions from fossil fuel combustion are necessary. The intensified use of coal would substantially increase the emissions of CO_2 unless there was very widespread deployment of carbon capture and storage [3]. Carbon dioxide capture is generally estimated to represent three-fourths of the total cost of a carbon capture, transport and sequestration system. Among the different capture concepts, Chemical-Looping Combustion (CLC) is one of the most promising technologies to carry out the CO_2 capture with low cost and small efficiency loss.

CLC is based on the transfer of the oxygen from air to the fuel by means of a solid oxygen-carrier. CLC technology has been widely proven using two interconnected fluidized beds: the fuel reactor and the air reactor [4]. In the fuel reactor the fuel is oxidized through reduction of the oxygen-carrier. The oxygen-carrier is transported to the air reactor where is regenerated by oxidation with air. The stream of combustion gases from the fuel reactor contains primarily CO_2 and H_2O. Water can be easily separated by condensation and a highly concentrated stream of CO_2 ready for compression, transport and sequestration is achieved. The gas stream from the air reactor is oxygen-depleted and consists only in N_2 and some unreacted O_2. Thus, N_2 in air is not mixed with the combustion gases and inherent separation of CO_2 from other gases is performed with no costs or energy penalty for gas separation.

Chemical Looping Combustion (CLC) with gaseous fuels has been developed in the last few years, but using CLC with solid fuels has shown to have recently a great interest [5]. The use of coal in CLC is very attractive in future sceneries with restriction in CO_2 emissions, since coal will keep on being a main energy source in the medium-term. One option for CLC with solid fuels is directly to introduce coal in the fuel-reactor, which is fluidized by a

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Nomenclature

C_C	char concentration in the fuel reactor bed
$F_{CO_2,in}$	CO_2 flow introduced in the fuel reactor (mol/s)
$F_{C,AR}$	carbon flow in char that enters the air reactor (mol/s)
$F_{C,g}$	gasified carbon flow exiting as part of the product gas (mol/s)
$F_{C,in}$	carbon flow in char fed with the fuel flow (mol/s)
$F_{C,out}$	carbon flow in char leaving the fuel reactor (mol/s)
$F_{C,r}$	carbon flow in char recirculated back to the fuel reactor (mol/s)
$F_{H_2O,in}$	H_2O flow introduced in the fuel reactor (mol/s)
$F_{H_2O,out}$	molar gas flow of H_2O in the product gas (mol/s)
F_i	molar gas flow of each component i (CO_2, CO, H_2 or CH_4) in the product gas (mol/s)
F_{ilm}	ilmenite flow between reactors (mol/s)
F_{N_2}	downstream introduced N_2 flow (mol/s)
F_{out}	total dry basis outlet gas flow (mol/s)
m	instantaneous mass of the ilmenite sample (kg)
m_C	mass of char in the fuel reactor bed (kg)
Me_xO_y	oxidized form of the oxygen carrier
Me_xO_{y-1}	reduced form of the oxygen carrier
m_{ilm}	ilmenite inventory in the fuel reactor (kg/MW$_{th}$)
m_o	mass of the oxidized form of the oxygen carrier (kg)
m_r	mass of the reduced form of the oxygen carrier (kg)
$N_{0,ilm}$	molar amount of oxygen in ilmenite active for CLC process (mol)
$N_{C,char}$	mol number of carbon fed into the reactor (mol)
$R_{0,ilm}$	oxygen transport capacity of ilmenite
$r_C(t)$	rate of char conversion (mol/s)
$r_{C,inst}$	instantaneous rate of char conversion (s^{-1})
$r_O(t)$	rate of oxygen transferred from ilmenite to the fuel gas (mol/s)
t	time (s)
t_{50}	time to convert 50% char (s)
t_{95}	time to convert 95% char (s)
t_X	residence time to reach a conversion X_t
X_{char}	char conversion
X_{ox}	conversion of ilmenite for the oxidation reaction
X_{red}	conversion of ilmenite for the reduction reaction
X_t	char conversion reached with a residence time t_X
y_i	being the molar fraction of the component i (CO_2, CO, H_2 or CH_4) in the product gas
η_{CS}	carbon stripper efficiency
η_C	combustion efficiency

gasification agent [6–9]. The reactor scheme of Chemical-Looping Combustion of solid fuels is shown in Fig. 1. In this technology coal is physically mixed with the oxygen-carrier in the fuel reactor where H_2O and/or CO_2 are used as fluidizing gas and gasifying agent. Thus, different processes are happening simultaneously in the reactor: (i) the pyrolysis and gasification of coal, where CO and H_2 are the main product, proceed according reactions (1)–(3); and (ii) the reaction of volatiles and gasification products with the oxygen-carrier to give CO_2 and H_2O, according reaction (4). The oxygen-carrier reduced in the fuel reactor, Me_xO_{y-1}, is transferred to the air reactor where reaction (5) with oxygen from air takes place. Thus the oxygen-carrier is regenerated to start a new cycle. The net chemical reaction is the same as usual combustion with the same combustion enthalpy.

$$\text{Coal} \rightarrow \text{Volatile matter} + \text{Char} \tag{1}$$

$$\text{Char} + H_2O \rightarrow H_2 + CO \tag{2}$$

$$\text{Char} + CO_2 \rightarrow 2CO \tag{3}$$

$$n\text{Me}_x\text{O}_y + H_2, CO, \text{Volatile matter(e.g.}CH_4) \\ \rightarrow n\text{Me}_x\text{O}_{y-1} + CO_2 + H_2O \tag{4}$$

$$\text{Me}_x\text{O}_{y-1} + 1/2O_2 \rightarrow \text{Me}_x\text{O}y \tag{5}$$

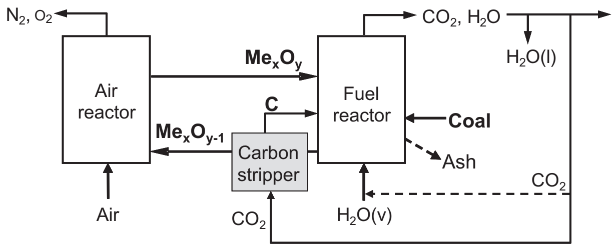

Fig. 1. Reactor scheme of Chemical-Looping Combustion using solid fuels (--- optional stream).

The gasification process is expected to be the slower step in the fuel reactor, thus the mean residence time for char particles in the fuel reactor should be higher than for oxygen-carrier particles. To increase the mean residence time of char and to avoid unreacted carbon entering the air reactor, the char particles can be separated from the oxygen-carrier in a so-called carbon stripper and re-introduced to the fuel reactor.

The possibility of using the CLC technology for solid fuels has been showed at laboratory scale using different oxygen-carrier materials – e.g. Cu- or Fe-based particles, and different solid fuels – e.g. coal, biomass, solid wastes, pet-coke [7–10]. After the encouraging results obtained at laboratory scale, the feasibility of the CLC process for solid fuels in a continuously operated prototype was proven by Berguerand and Lyngfelt [11,12] using ilmenite as oxygen-carrier. A carbon stripper was designed between the fuel reactor and the air reactor to increase the residence time of char particles in the fuel reactor. Due to the characteristics of this facility, the volatiles do not get in contact with oxygen-carrier particles. Thus, only the conversion of gases from steam gasification (CO and H_2) was analyzed. The importance of using high temperatures in this process was acknowledged [13] in order to have high conversion of the solid fuel to gases into the reactor. Also the effect of the mean residence time of char particles – determined by the solids circulation flow-rate – on its conversion in the fuel reactor was analyzed [14]. A higher circulation of solids reduced the mean residence time in the reactor and thus a lower efficiency of gasification was obtained. In general, high carbon capture efficiencies can be reached (82–96%) [11]. However, some fraction of unconverted gases (CO and H_2) were obtained in the outlet stream, which demanded about 5–7% of the total oxygen necessary to burn coal to CO_2 and H_2O when the fuel reactor temperature was 1000 °C [13]. Furthermore, Cuadrat et al. [15] investigated the effect of operating conditions such as temperature and coal particle size on the combustion efficiency as well as on the extent of gasification in a continuous CLC rig. In this case, volatiles were generated inside the bed. Values for the oxygen demand of gases from 5% to 15% were found in all the experimental work, mainly due to unconverted CO and H_2 coming from devolatilization process. Nevertheless,