Numerical assessment of the effects of carbon deposition and oxidation on chemical looping combustion in a packed-bed reactor

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ARTICLE INFO

ABSTRACT

Chemical looping combustion with methane as fuel in a packed-bed reactor using Ni as oxygen carrier was numerically investigated. To this aim, a mathematical model that takes into account both oxidation and reduction phases was developed. To describe catalyst fouling due to carbon deposition, CH_4 decomposition and carbon regasification by steam and CO_2 (Boudouard reaction) were considered during reduction phase, while carbon combustion was taken into account during oxidation phase. A catalyst deactivation function due to carbon accumulation on oxygen carrier was introduced too. In the paper the effects of fouling on the operability of packed-bed reactor was studied, focusing the attention on the switch strategy adopted. Results show that a detailed description of carbon deposition and consumption phenomena is an essential prerequisite to properly operate a CLC process. Indeed, it was found that working with variable oxidation and reduction time lengths, the power produced is about three times greater than of that obtainable operating with fixed times. Although carbon deposition can be also reduced by increasing the $H_2O:CH_4$ feed ratio, it was found that in this case the power produced decreases by about 30% with respect to that obtained operating with variable oxidation and reduction time lengths.

1. Introduction

Carbon dioxide (CO_2) is one of the most significant contributors to greenhouse effect and nowadays its emissions keep growing, albeit at a slower pace than in the past (IEA, 2015). Although anthropogenic CO_2 emissions mainly arise from the utilization of fossil fuels for energy production, other industrial processes, such as cement and steel production, give relevant contributions too. As a consequence, more and more interest on Carbon Capture and Sequestration (CCS) technologies for the containment of CO_2 emissions from stationary sources has kept growing over the last years (Agency, 2015; Olivier et al., 2012).

CCS generally involves three different steps, namely CO_2 capture, transport and storage, the first one generally being the most energy-intensive step of the process (Adanez et al., 2012). Among different CO_2 capture technologies, Chemical-Looping Combustion (CLC) allows both power productions and CO_2 capture; CLC is a cyclic unmixed combustion process that relies on an Oxygen Carrier (OC), usually a particulate metallic solid, capable of being alternatively reduced and oxidized: ultimately, the effect of CLC is the conversion of fuel to CO_2 and H_2O, while the OC swings back and forth from the reduced to the oxidized state. Due to the features of the process, the CO_2 containing stream produced during the OC reduction step is N_2-free and therefore can be easily purified and sequestered. Moreover, CLC occurs without NOx formation (Agency, 2015).

Interconnected fluidized bed reactors, with a wide array of configurations, were proposed for CLC (e.g. Lyngfelt et al., 2001; Adanez et al., 2006; Abad et al., 2007; Kolbitsch et al., 2009). As a feasible alternative to fluidized bed, packed-bed reactors were suggested (Noorman et al., 2007), although both a careful heat management strategy and switching valves able to work at very high temperature were needed in order to operate such a system (Fernandez and Abanades, 2014).

In CLC processes, whatever the adopted technology, superficial properties of OC play a significant role, since the carrier itself acts as a catalyst during the fuel oxidation step (Adanez et al., 2012). Generally, the metal is introduced in the reactor impregnated on porous catalyst particles, typically Ni on γ-Al_2O_3, α-Al_2O_3, $MgAl_2O_4$ or $CaAl_2O_4$ (Gayan et al., 2008). As with all catalytic processes dealing with hydrocarbons, catalyst fouling due to carbon deposition, and consequent deactivation and reactivity loss over time, is a serious problem (e.g. see Bartholomew (2001)). In CLC processes carbon fouling becomes appreciable only when more than 80% of the oxygen available on the catalyst surface is consumed and this problem is particularly significant

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Nomenclature

a_0	initial specific surface area of the oxygen carrier, $\mathrm{m^2\,kg_{OC}^{-1}}$
$C_{NiO}^{0'}$	initial NiO concentration, $\mathrm{mol_{NiO}\,kg^{-1}_{OC}}$
$C_{N_2}^0$	initial concentration of N_2, $\mathrm{mol\,m^{-3}}$
C_{Ni}^0	initial concentration of Ni, $\mathrm{kg_{Ni}\,kg^{-1}_{OC}}$
C_C	carbon concentration, $\mathrm{kg_C\,kg^{-1}_{OC}}$
$C_{i,in}$	inlet concentration of species i, $\mathrm{mol\,m^{-3}}$
C_i	concentration of species i, $\mathrm{mol\,m^{-3}}$
C_{NiO}	concentration of NiO, $\mathrm{kg_{Ni}\,kg^{-1}_{OC}}$
C_{Ni}	concentration of Ni, $\mathrm{kg_{Ni}\,kg^{-1}_{OC}}$
c_{pg}	heat capacity of the gas stream, $\mathrm{J\,kg^{-1}\,K^{-1}}$
C_{tot}	total gas concentration, $\mathrm{mol\,m^{-3}}$
$D_{ax,i}$	axial dispersion coefficient of species i, $\mathrm{m^2\,s^{-1}}$
d_p	particle diameter, m
d_t	reactor internal diameter, m
k_1	kinetic parameter of carbon oxidation reactions, $\mathrm{s^{-1}\,Pa^{-1}}$
k_2	kinetic parameter of carbon oxidation reactions, $\mathrm{s^{-1}\,Pa^{-1}}$
k_3	kinetic parameter of carbon oxidation reactions, $\mathrm{s^{-1}}$
L	bed length, m
M_i	molecular weight of species i, $\mathrm{kg\,mol^{-1}}$
P_i	partial pressure of species i, Pa
Q	gas volumetric flow rate, $\mathrm{m^3\,s^{-1}}$
R	ideal gas constant, $\mathrm{J\,mol^{-1}\,K^{-1}}$
r_i	the rate of consumption or formation of species i, $\mathrm{mol\,kg_{OC}^{-1}\,s^{-1}}$
r_{RJ}	rate of reaction j per unit mass of the oxygen carrier, $\mathrm{mol\,kg_{OC}^{-1}\,s^{-1}}$
T	temperature, K
t	time, s
T_p	period, s
T_{in}	inlet temperature, K
u_r	non-catalytic reduction reactions front velocity in Eq. (3), $\mathrm{ms^{-1}}$
u_{sg}	superficial gas velocity, $\mathrm{ms^{-1}}$
V_c	volumetric heat capacity, $\mathrm{J\,m^{-3}\,K^{-1}}$
X	NiO conversion degree
y_i	molar fraction of specie i
z	spatial variable, m

Greek symbols

α_c	deactivation constant, $\mathrm{kg_{OC}\,kg^{-1}_C}$
β	H_2O:CH_4 ratio
ΔH_j	reaction enthalpy of reaction j, $\mathrm{J\,mol^{-1}}$
λ_{eff}	effective heat conductivity, $\mathrm{W\,m^{-1}\,K^{-1}}$
ν	signal feed control
Φ	deactivation function in Eq. (4)
Ψ	stoichiometric coefficient of carbon oxidation reaction in Eq. (2)
ρ_g	gas density, $\mathrm{kg\,m^{-3}}$
ρ_{OC}	packed-bed density, $\mathrm{kg_{OC}\,m^{-3}}$
ε_g	bed porosity
ξ	dimensionless axial position z/L

Subscipts

i	solid and gas species CH_4, H_2O, H_2, CO, CO_2, N_2, O_2, Ni, NiO, C index
j	chemical reaction index
k	cycle index
oxi	oxidation
out	outlet elemental carbon
red	reduction
supply	fed elemental carbon

Abbreviations

CCS	carbon capture and sequestration
CLC	chemical looping combustion
OC	oxygen carrier
OP	oxidation phase
RP	reduction phase

when the processes are carried out in packed-bed (Hossain and De Lasa, 2008). However, the possibility exists of removing deposited carbon during Oxidation Phase (OP), completely regenerating the OC, but this depends on the physical nature of the accumulated carbon. Three different deposited carbon types were reported in catalytic steam methane reforming on a Ni-based catalyst, namely encapsulating hydrocarbon films, whiskerlike carbon and pyrolytic carbon (Bartholomew, 1982). The type of deposited carbon mainly depends on the operating conditions of the process (e.g operating temperature, physical nature of oxygen carrier, etc.) and all three types listed above may or may not be simultaneously present. Claridge et al. (1993) investigated carbon deposition on different catalysts used for CH_4 partial oxidation, reporting that both whiskerlike and encapsulated forms of carbon were formed on OC. Snoeck et al. (1997), Ito et al. (1999) and Mendiara et al. (2011) reported that filamentous whisker-like carbon is mainly formed in the conditions typical of steam and dry reforming. Another important issue that emerges from the above mentioned studies is that these three forms have a very different reactivity with oxygen. In particular, whiskerlike form is characterized by the highest reactivity with air compared to encapsulating hydro-carbons film and pyrolytic carbon (Ito et al., 1999; Mendiara et al., 2011).

Although there are many papers dealing with carbon fouling of catalyst particles, effects of carbon deposition on cyclically operated chemical-looping combustion in a packed-bed received limited atten-tion: Jin and Ishida (2002) studied the reactivity of natural-gas-fueled chemical-looping combustion with $NiO/NiAl_2O_4$ as carrier, verifying with a thermogravimetric analysis that no carbon on the surface of OC was detected after more than 20 redox cycles; Chiron et al. (2011) analyzed H_2 production by chemical-looping reforming using methane as fuel, experimentally detecting CO and CO_2 at the outlet of packed-bed during OP, thus proving that the carbon deposited during the previous Reduction Phase (RP) was oxidized by air; Silvester et al. (2015) studied two different supports as NiO based oxygen carriers for CLC with methane as fuel and observed simultaneous weight loss of OC and CO_2 production during regeneration of catalyst with air, proving that carbon deposited during the fuel oxidation phase is amenable to be oxidized by air; moreover, they found that the final weight of OC after OP was the same of the fresh catalyst, confirming that all deposited carbon could be removed; Jiang et al. (2015) investigated H_2 produc-tion in a packed-bed using NiO/Ni as oxygen carrier and glycerol as fuel, verifying the absence of whiskerlike filamentous carbon on the catalyst after several experimental runs. There are, indeed, cases when the regeneration of the bed with a stream of air could not remove all of the deposited carbon, as discussed by Giannakeas et al. (2012) for H_2 production by chemical looping in a packed-bed. It is important to stress, however, that these authors did not use methane as fuel, but scrap type oil.

The literature analysis reported above shows that, under the typical conditions in which CLC processes are operated in packed-bed and using CH_4 as fuel, the carbon with highest reactivity with air, i.e. whiskerelike form, is deposited on the surface of OC during RP and that