Simulation of hydrogen production through chemical looping reforming process in a packed-bed reactor

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ABSTRACT

In the present work the numerical analysis of an autothermal chemical looping reforming (CLR) packed-bed reactor for hydrogen production is presented. The reactor works with Ni-based oxygen carriers, methane is used as fuel and continuous cyclic operations are simulated. The proposed process poses a number of challenges, namely the choice of the time-length of oxidation and reduction phases, the start-up temperature and the cycle design. This paper theoretically quantifies these challenges through numerical simulations. A 1D numerical reactor model, validated by comparison with experimental data available in literature, was developed. Results for the cyclic process are presented, and the effects on the feasibility of the process of a variation in operating conditions are discussed. It is concluded that an appropriate choice of both the initial temperature and the length of oxidation and reduction phases is essential prerequisite for the process feasibility and performances.

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1. Introduction

The increase in CO_2 atmospheric concentration deriving from anthropic activities greatly contributes to "greenhouse effect" and therefore to global warming. Given that the majority of CO_2 emissions come from power plants burning fossil fuels for power generation in industry (Solomon et al., 2007), one of the targets of the "Europe 2020" strategy launched by the European Union in early 2010 is to decrease CO_2 emissions. Carbon Capture and Storage (CCS) technologies are valid options to reduce net CO_2 emissions. However, the main problem of these techniques is that, due to the high nitrogen concentration in air, the initial CO_2 separation step demands significant amounts of energy (Change, 2005). Chemical-looping combustion (CLC), combining power production with CO_2 capture, represents one of the most promising CO_2 emission reduction technologies with low energy penalty (Adanez et al., 2012). CLC consists in

a cyclic unmixed combustion process, where a metal oxide is used as an oxygen carrier in order to, at first, oxidize a fuel, and then to be re-oxidized in air; as a consequence, no direct contact between fuel and combustion air occurs and a N_2-free CO_2 rich steam is produced, ready for separation. However, CCS technologies cannot be applied to transport sector, despite the fact that it represents the second biggest greenhouse gas emissions source (Solomon et al., 2007): the use of hydrogen as fuel is one of the most promising ways to reduce greenhouse gas emissions from vehicles (Edwards et al., 2008), although molecular hydrogen is not a primary source and needs to be produced. While some indications exist that in the future the main source of hydrogen could be water (with electricity coming either from renewable sources or from nuclear power stations), at present the main route for hydrogen production is the chemical treatment of hydrocarbons, via steam reforming of methane/light hydrocarbons,

Nomenclature

a_0	initial specific surface area of the oxygen carrier ($m^2\,kg^{-1}_{carrier}$)
C_i	concentration of species i ($mol\,m^{-3}$)
$C_{i,in}$	inlet concentration of species i ($mol\,m^{-3}$)
C^0_{N2}	initial concentration of N_2 ($mol\,m^{-3}$)
C^0_{Ni}	initial concentration of Ni ($mol\,m^{-3}$)
C'^0_{NiO}	initial NiO concentration ($mol\,kg^{-1}_{carrier}$)
c_{pg}	heat capacity of the gas stream ($J\,mol^{-1}\,K^{-1}$)
c_{ps}	heat capacity of solid ($J\,mol^{-1}\,K^{-1}$)
$D_{ax,i}$	axial dispersion coefficient of species i ($m^2\,s^{-1}$)
$D_{e,i}$	effective diffusion coefficient of species i ($m^2\,s^{-1}$)
$D_{K,i}$	Knudsen diffusion coefficient of species i ($m^2\,s^{-1}$)
$D_{m,i}$	diffusion coefficient of species i in the mixture ($m^2\,s^{-1}$)
d_p	particle diameter (m)
d_t	reactor internal diameter (m)
E_1	activation energy of equilibrium constant ($J\,mol^{-1}\,K^{-1}$)
$E_{ai,j}$	activation energy of adsorption coefficient of specie i in reaction j ($J\,mol^{-1}$)
$E_{a,j}$	activation energy of reaction rate of reaction j ($J\,mol^{-1}$)
$E_{a,si}$	activation energy of non-catalytic gas–solid reactions ($J\,mol^{-1}$)
E_{aPJ}, E_2	activation energy of equilibrium constant ($J\,mol^{-1}$)
G	mass flux of the gas phase ($kg\,m^{-2}\,s^{-1}$)
i	gas phase species (CH_4, H_2O, H_2, CO, CO_2, N_2, O_2) index
h_f	gas–solid heat transfer coefficient ($J\,s^{-1}\,m^{-2}\,K^{-1}$)
j	chemical reaction index
$K_{CH4,R9}$	adsorption coefficient of CH_4 (methane decomposition) (bar^{-1})
$K_{CH4,R10}$	adsorption coefficient of CH_4 (carbon gasification by H_2O) (bar^{-1})
$K_{CO,R6}$	adsorption coefficient of CO (steam reforming) (bar^{-1})
$K_{CO,R11}$	adsorption coefficient of CO (carbon gasification by CO_2) (bar^{-1})
$K_{CO2,R11}$	adsorption coefficient of CO_2 (carbon gasification by CO_2) (bar)
$K_{H2,R6}$	adsorption coefficient of H_2 (steam reforming) ($bar^{-0.5}$)
$K_{H2,R9}$	adsorption coefficient of H_2 (methane decomposition) ($bar^{1.5}$)
$K_{H2,R10}$	adsorption coefficient of H_2 (carbon gasification by H_2O) ($bar^{1.5}$)
$K_{H2O,R6}$	adsorption coefficient of H_2O (steam reforming) (–)
$K_{H2O,R10}$	adsorption coefficient of H_2O (carbon gasification by H_2O) (–)
$K_{i,Rj,0}$	pre-exponential factor of adsorption coefficient of specie i in reaction j
$K_{P,R6}$	equilibrium constant of SR (bar^2)
$K_{P,R8}$	equilibrium constant of WGS ($mol\,kg^{-1}_{Ni}\,s^{-1}\,bar$)

$K_{P,R9}$	equilibrium constant of methane decomposition (bar)
$K_{P,R10}$	equilibrium constant of carbon gasification by H_2O (bar)
$K_{P,R11}$	equilibrium constant of carbon gasification by CO_2 (–)
$K_{P,Rj,0}$	pre-exponential factor of equilibrium constant
k	cycle index
kf	gas–solid mass transfer coefficient ($m\,s^{-1}$)
k_{R6}	reaction rate constant of SR $mol\,kg^{-1}_{Ni}\,s^{-1}\,bar^{-0.25}$)
k_{R7}	reaction rate constant of DR ($mol\,kg^{-1}_{Ni}\,s^{-1}\,bar^{-2}$)
k_{R8}	reaction rate constant of WGS ($mol\,kg^{-1}_{Ni}\,s^{-1}\,bar^{-1}$)
k_{R9}	reaction rate constant of methane decomposition ($mol\,kg^{-1}_{Ni}\,s^{-1}$)
k_{R10}	reaction rate constant of carbon gasification by H_2O ($mol\,kg^{-1}_{Ni}\,s^{-1}$)
k_{R11}	reaction rate constant of carbon gasification by CO_2 ($mol\,kg^{-1}_{Ni}\,s^{-1}$)
$k_{Rj,0}$	pre-exponential factor of reaction rate constant
k_{si}	chemical reaction rate constant ($m\,s^{-1}$)
$k_{si,0}$	pre-exponential factor of non-catalytic gas–solid reactions ($J\,mol^{-1}$)
L	bed length (m)
L_e	Lewis number ($J\,m^{-3}\,K$)
M_{act}	molecular weight of the active material in the solid ($kg\,mol^{-1}$)
M_i	molecular weight of i species, ($kg\,mol^{-1}$)
N_{Me}	Mears number for interphase mass gradient (–)
N_{Met}	Mears number for interphase temperature gradient (–)
N_{WP}	Weisz–Prater number (–)
P	total pressure (Pa)
P_i	partial pressure of species i (Pa)
Q	flow rate ($m^{-3}\,s$)
R	ideal gas constant ($J\,mol^{-1}\,K^{-1}$)
Re	Reynolds number (–)
r_i	the rate of consumption or formation of species i ($mol\,kg^{-1}_{carrier}\,s^{-1}$)
r_{obs}	observed reaction rate ($mol\,m^{-3}\,s^{-1}$)
r_{Rj}	rate of reaction j per unit mass of the oxygen carrier ($mol\,kg^{-1}_{carrier}\,s^{-1}$)
Sc	Schmidt number (–)
T	temperature (K)
$\tilde{T}$	period (s)
T_0	initial temperature of the bed for the first oxidation phase (K)
T_{in}	inlet temperature (K)
T_{amb}	ambient temperature (K)
T_{max}	maximum temperature reachable in the bed (K)
t	time (s)
t_{oxi}	oxidation time (s)
t_{red}	reduction time (s)
u_{sg}	superficial gas velocity ($m\,s^{-1}$)
V_{fr}	velocity of reaction front ($m\,s^{-1}$)
V_{th}	velocity of thermal front ($m\,s^{-1}$)
w_{act}	weight fraction of the reactive material in the solid ($kg\,mol^{-1}$)