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Model-based analysis of bench-scale fixed-bed units for chemical-looping combustion

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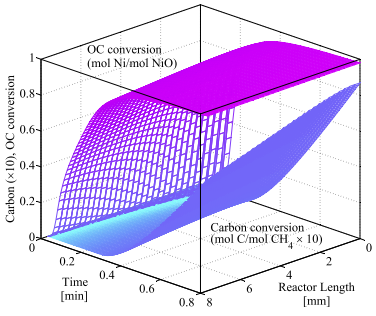
HIGHLIGHTS

- Model-based analysis of fixed bed CLC systems operating with NiO and CH_4.
- Universal kinetics for NiO reduction and Ni catalyzed reactions at CLC conditions.
- Modified volumetric model predicts accurately CH_4 activation and CH_4 slip in CLC.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this work is to compare reaction schemes and kinetic mechanisms, and simulate the dynamic behavior of chemical-looping Reducers operating with methane as the feed and nickel oxide as the oxygen carrier. A dynamic model for the reduction step of chemical-looping combustion in fixed-bed reactors is developed, on the basis of the same kinetic network to predict published experimental data of different fixed-bed reactors and data of a chemical-looping fixed-bed reactor operating at the University of Connecticut. Steam reforming, water gas shift, dry reforming, methane decomposition, and carbon gasification by carbon dioxide and steam are considered as reactions catalyzed by the reduced oxygen carrier. Heterogeneous reactions of the oxygen carrier encompass reactions with methane, carbon monoxide and hydrogen. Kinetic expressions reported in the literature are compared and their parameters are estimated on the basis of experimental data of nickel-based oxygen carriers for chemical-looping combustion of methane. Particle shrinking, molar expansion and surface area changes are accounted for in the transient plug flow reactor model. The applicability of the shrinking core and modified volumetric models, which are typically used for the description of gas–solid reactions is verified and compared against various experimental data, showing the superiority of the latter. A global mechanism and kinetic parameters that can be used to simulate CLC Reducers operating with NiO as the oxygen carrier and CH_4 as the fuel are proposed. Finally, discrepancies between published data and the model accuracy for different experimental setups are discussed.

1. Introduction

Chemical-looping combustion (CLC) is a method for the oxidation of hydrocarbons with *in situ* O_2 separation, resulting in energetically inexpensive CO_2 sequestration. The basic concept of the process involves two interconnected reactors, a Reducer and an Oxidizer, with an oxygen carrier (OC) – a metal/metal oxide – circulating between the two (Fig. 1). In the Reducer, hydrocarbons are oxidized by the lattice oxygen of the OC, that is a metal oxide – Me_xO_y, which in turn is reduced to a lower oxidation state (M_yO_{x-z}). The reduced oxygen carrier is then re-oxidized in the Oxidizer. The exhaust gas stream of the Reducer contains CO_2, CO, H_2, H_2O and minimal N_2, depending on the process operating

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Nomenclature

a_0	initial specific area of the oxygen carrier, $m^2/kg_{carrier}$
C_i	bulk concentration of gaseous reactant, $kmol/m^3$
C_I	concentration of inert gas, $kmol/m^3$
C_{CH_4}	concentration of CH_4, $kmol/m^3$
C'_{NiO}	initial NiO concentration, $mol_{NiO}/kg_{carrier}$
C_{Ni}	Ni concentration, $kg_{Ni}/kg_{carrier}$
C_{NiO}	NiO concentration, $kg_{NiO}/kg_{carrier}$
D_i	dispersion coefficient
Ea_j	activation energy, kJ/mol
i	species
j	reaction
$k_2 - k_5, k'_2 - k'_4$	rate constant
$k_{j,0}$	pre-exponential factor of rate constants k_j
$K_{CO,j}$	adsorption coefficient of CO, bar^{-1}
$K_{CO_2,j}$	adsorption coefficient of CO_2, bar
$K_{CH_4,j}$	adsorption coefficient of CH_4, bar^{-1}
$K_{H_2,6}$	adsorption coefficient of H_2, bar^{-1}
$K_{H_2,9}$	adsorption coefficient of H_2, $bar^{3/2}$
$K_{H_2O,j}$	dissociate adsorption coefficient of H_2O
$K_{i,j,0}$	pre-exponential factor of adsorption coefficient, $K_{i,j}$
$K_{j,0}$	pre-exponential factor of equilibrium constant, K_j
K_6, K_8	equilibrium constants for steam reforming and dry reforming, bar^2
K_7	equilibrium constant for WGS
K_9, K_{10}, K_{11}	equilibrium constants for methane decomposition, carbon gasification by H_2O and CO_2, bar
k_6	rate constants for steam reforming, $bar^{0.5}mol/g_{Ni}/s$
k_7, k_8	rate constants for WGS and dry reforming, $mol/bar/g_{Ni}/s$
k_9	rate constant for methane decomposition, bar^{-1}
k_{10}, k_{11}	rate constants for carbon gasification by H_2O and CO_2, $mol/g_{Ni}/s$
M_i	molecular weight, kg/kmol
n_j	reaction order
P	total pressure, bar
P_i	partial pressure, bar
r_g	grain radius, m
r_j	rate for reaction j, $mol/g_{Ni}/s$
R	gas constant, J/mol/K
t	time, s
T	temperature, K
u_{sg}	gas superficial velocity, m/s
W^0_{NiO}	initial NiO concentration, $kg_{NiO}/kg_{carrier}$
X	NiO conversion
z	reactor coordinate, m

Greek letters

$\Delta H_{j,0}$	enthalpy change of reaction j, kJ/mol
$\Delta H_{i,j,0}$	enthalpy change of species i adsorption for reaction j, kJ/mol
ε_g	gas holdup
ρ_m	molar density of OC, mol/m^3
ρ_{OC}	density of OC, kg/m^3

conditions, feedstock composition, and OC selectivity. Therefore, the main principle in chemical-looping is the oxidation of hydrocarbons with a metal oxide in a N_2-free environment. Chemical-looping has the potential to make carbon capture significantly more efficient than current systems. However, it is still at an early stage of development, with challenges in material handling and oxygen carrier selection [1,2]. In particular, the National Energy Technology Laboratory (NETL) [3] of the U.S. Department of Energy classifies CLC as the most promising technology in terms of cost reduction and process efficiency, while underscoring that more time is required for its commercialization [4].

Ni-based OCs have been extensively analyzed [5]. Under typical CLC temperatures, Ni-based OCs show very high reactivity and performance. High oxidation rates of CH_4 can be achieved with NiO, although small amounts of H_2 and CO are detected at the exit of the Reducer because of thermodynamic restrictions [6]. One drawback of Ni is that it is more expensive than other oxygen carriers, like Cu and Fe. Also, due to the toxicity of Ni, additional precautions must be taken. Moreover, Ni can trigger carbon formation reactions, which are not favorable in CLC, because carbon is transferred with the solids to the Oxidizer, reducing the process CO_2 separation efficiency. Nevertheless, because NiO-based OCs have been widely used in CLC and an abundance of NiO-based CLC experimental data are reported, it is of interest to study CLC kinetics involving NiO/Ni.

Different configurations have been proposed for CLC: interconnected fluidized beds, including riser and bubbling fluidized beds [7], two bubbling fluidized beds [8] or dual circulating fluidized beds [9], and periodically operated fixed-beds [10,11]. As discussed by Fan and Li [12], the development of the CLC technology is highly dependent on understanding the intricate interrelationships between reaction and process engineering factors. CLC modeling can facilitate the grasp of these relationships and help to design, optimize, and scale up the CLC processes. CLC process simulation can be performed on different levels of accuracy with differing methodologies and varying computational costs. The modeling ap-

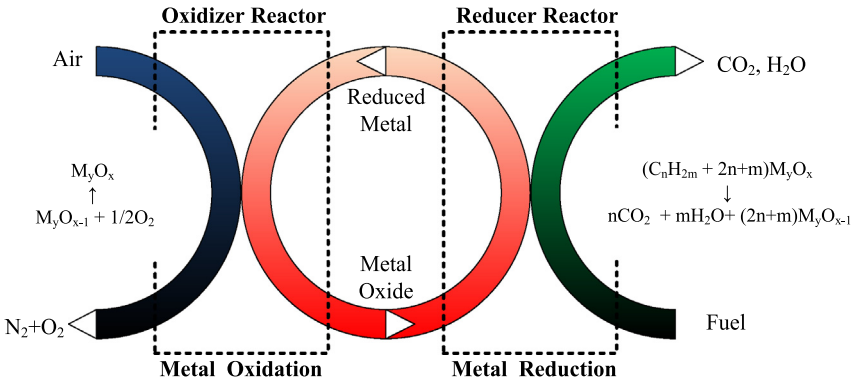

Fig. 1. Basic concept of chemical-looping combustion process.