



Full Length Article

Multi-fluid reactive modeling of sorption enhanced steam reforming of coke oven gas in fluidized bed

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HIGHLIGHTS

- Modeling of sorption enhanced steam reforming of coke oven gas in pilot-scale fluidized bed.
- A three-fluid Eulerian model coupling with structure-dependent chemical kinetics was presented.
- H₂ in COG augmented suppression of high operational pressure on carbon conversion.
- T > 580 °C, S/C = 3.3–4.3 and C/A = 0.2–1 was essential to achieve CH₄ conversion >80%.

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ABSTRACT

A three-fluid Eulerian approach, which couples structure-dependent kinetic models of catalysis and carbonation reactions, is used to model sorption-enhanced steam reforming of coke oven gas (SER-COG) in a pilot-scale fluidized bed reactor. Three pellet models (PM-I, PM-II, PM-III) in terms of methodologies coupling hydrodynamics of multiple fluids with multi-scale reactions were comparatively studied. Pellet model PM-I, which dealt with catalyst and sorbent as separate dispersion phases and linked reaction kinetics closely with micro-structures of pellets in corresponding disperse phase, well reproduced the reformed gas compositions observed in experiments. With pellet model PM-I incorporated with the three-fluid Eulerian approach, numerical studies demonstrated that high H₂ or CO inlet fraction would suppress conversion of CH₄, and decreased CO selectivity because of the reduced reforming rates of steam and methane. High initial H₂ fraction in COG also amplified the suppression of high operational pressures on SER-COG. To achieve CH₄ conversion > 90%, products with H₂ > 95% and CO < 1%, a C/A (mass) of 0.2–1, steam/CH₄ around 3.3–4.3 were suggested for atmospheric SER-COG at 580 °C when a mixture of H₂/CH₄/CO (0.3:0.6:0.06, molar) was fed as fuel.

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1. Introduction

Coke oven gas (COG) is a byproduct of coke-making process. It mainly consists of combustible gases such as CO, H₂ and CH₄, and non-combustible gases including CO₂ and N₂ [1]. Typically, the mole fraction of H₂ amounts to 54–59%, and CH₄, CO may take up 24–28% and 6–8% respectively in COG. The annual production of COG in China exceeds 1800 Nm³. However, over half of COG is burned as waste gas or discharged directly [1]. Therefore, production of hydrogen from COG was attractive for energy saving and reduce environmental pollution [2].

Pressure swing adsorption (PSA) separation was the major approach to recover H₂ from COG, but only hydrogen contained in COG may be separated. The remaining CH₄, CO and C₂+ hydrocarbons were usually fueled to a combustor or also released into the atmosphere. Therefore, chemical methods to enhance conversion of tar, CH₄ and CO in COG, such as steam reforming, partial oxidation and dry reforming, have been applied to amplify the H₂ recovery ratio from COG [1]. Catalytic steam reforming of COG (SR-COG) is more favorable for hydrogen production, because hydrogen not only can be produced from COG but also steam. However, SR-COG was seriously limited by thermodynamic equilibrium due to the high H₂ contents of COG, thus required a very high temperature exceeding 1000 °C to achieve complete conversion of CH₄ and CO [3]. To improve hydrogen yield at medium temperature, sorption-enhanced steam reforming of COG (SER-COG)

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Nomenclature

Latin symbol

C_{Ds}	drag coefficient for single spheric particles
D	diameter of cylinder reactor, m
D_e	efficient diffusion coefficient for gas, m ² /s
D_{pl}	CO ₂ diffusivity in product layer, m ² /s
D_{mol}	molecular diffusivity, m ² /s
D_{kn}	Knudsen diffusivity, m ² /s
d_p	particle diameter, m
e_{ss}	restitution coefficient of solid phase
g_0	radial distribution function
H_i	specific enthalpy of species i, J/kg
H_{sg}	interphase enthalpy between phase g and s (s = A, C), J/kg
h_{sg}	heat transfer coefficient between phases, w/(m ² K)
h	height on the fluidized bed, m
I	identity tensor
I_{2D}	second invariant of deviatoric stress tensor, s ⁻²
J_i	diffusion flux for species i, kg/(m ² s)
k_i	thermal conductivity of phase i (i = g, A, C), J/(m K s)
k_{eff}	effective thermal conductivity, J/(m K s)
k_{Θ}	diffusion coefficient of granular energy
m_{gs}	mass exchange between phase g and s (s = A, C), kg/(m ³ s)
Nu	Nusselt number
P	pressure, Pa
P_s	solid pressure, Pa
Pr	gas prandtl number
Q_{gs}	heat exchange between phases, w/s
Re	Reynolds number
T_i	temperature for phase i, K
U	superficial velocity, m/s
U_{mf}	minimum fluidization velocity, m/s

Greek symbol

$\alpha_{s,max}$	volume fraction for the particles at maximum packing
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Φ_{gs}	interphase kinetic energy exchange coefficient
β_{gs}	interphase momentum exchange coefficient
φ	specularity coefficient
ρ	density, kg/m ³
Θ	granular temperature, m ² /s ²
γ_s	collision dissipation energy
τ_i	stress tensor for phase i (i = g, A, C)
λ_s	bulk viscosity, kg/(m s)
μ_i	viscosity for phase i (i = g, A, C), kg/(m s)
$\mu_{s,col}$	collisional viscosity, kg/(m s)
$\mu_{s,kin}$	kinetic viscosity, kg/(m s)
$\mu_{s,fr}$	frictional viscosity, kg/(m s)

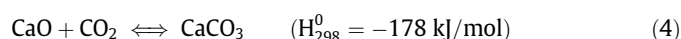
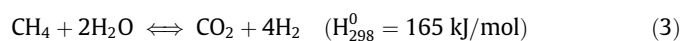
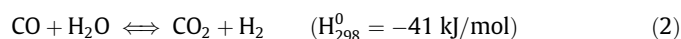
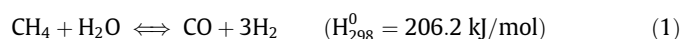
Subscript and superscript

g	gas phase
s	solid phase
A	adsorbent
C	catalyst
mf	minimum fluidization
b	bubble
col	collisional term
eff	effective term
kin	kinetic term
fr	friction term
in	interphase
0	initial condition

Abbreviations

SMR	steam methane reforming
$SE-SMR$	sorption enhanced steam reforming of methane
$SER-COG$	sorption enhanced steam reforming of coke oven gas
S/C	steam-to-methane ratio
C/A	catalyst-to-adsorbent ratio
IIG	incompressible ideal gas

was put forward. With CO₂ being captured on-line by an active sorbent during SER-COG, the chemical equilibrium of steam reforming of COG was shifted to the direction of hydrogen production [4]. The adsorbed CO₂ was then separated by desorption and gathered later for storage or other utilizations. CaO-based materials are ideal candidates as the sorbent due to their abundant sources [5], and fast kinetics and relative high CO₂ uptake at reforming temperature (500–850 °C). The main overall reactions in SER-COG process with CaO-based material as CO₂ acceptor were written as:



Incorporation of refractory materials such as MgO, ZrO₂, ZnO into CaO helped to inhibit sintering of CaO grains and stabilize the intra-particle pore structures, so improve its cyclic stability and mechanical properties [6,7]. Integration of CaO content and nickel-based catalyst chemically, named hybrid or bifunctional pellet, also can promote the cyclic stability of CaO [8–11]. In this

study, calcined dolomite, mainly consisting of MgO and CaO, was used as CO₂ acceptor during SER-COG in a pilot-scale fluidized bed reformer [7].

Steam reforming of COG amplified hydrogen volumetric content from 58.2% to 77.7%, but a reforming temperature >850 °C was required when only a NiO/MgO solid solution catalyst presented [12]. Wang et al. [13] conducted thermal economic, process efficiency analysis on SER-COG based on a thermodynamic equilibrium model. Compared with hydrogen recovery by PSA, energy conversion efficiency of SER-COG reached 77.6% at 2.5 MPa, S/C = 4.13, CaO/C = 1.75. Xie et al. [14] reported that SER-COG could convert the vast majority of carbon in COG into high purity CO₂ as by-product of hydrogen recovery. Wu et al. [15] experimentally studied SER-COG in a fixed bed reactor using a Ni-nano-CaO/Al₂O₃ sorption enhanced catalyst. A product with H₂ mole fraction >95% was achieved at 600 °C and a steam/CH₄ of 5.8 under atmospheric pressure [16]. Currently, rare work focused on SER-COG in a fluidized bed reactor, although fluidization operation was especially attractive for sorption-enhanced process because it facilitated continuous sorbent feed and regeneration. SER-COG in a fluidized reformer was an integration of multi-scale chemical reactions (catalysis, heterogeneous reactions), competition of adsorption and convection, and interfacial mass, heat and momentum transfer. Non-linear interaction of gas-solid phase, solid-solid phase also exerts vigorous effects on chemical reactions and physical transfer phenomena. Numerical studies of SER-COG based on multiphase

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