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Parametric study on catalytic tri-reforming of methane for syngas production

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ABSTRACT

A two-dimensional numerical model for syngas production from tri-reforming of methane (TRM) in adiabatic tubular fixed-bed reactors was established. From the results obtained, it was found that reactant must be preheated to certain temperatures for TRM activation. Although the delay factor accounting for the varying catalytic bed activities produced different temperature and species mole fraction profiles in the reactor upstream, the reactor performance was delay factor independent if the reactor outlet results were used because nearly identical temperature and species mole fraction variations were obtained at the reactor downstream. The numerical results also indicated that reverse water-gas shift reaction plays an important role for H_2 and CO yields. With higher O_2 in reactant, high temperature resulted, leading to lower H_2/CO ratio. The absence of H_2O in the reactant caused dry reforming of methane as the dominant reaction, resulting in H_2/CO ratio close to unity. With the absence of CO_2 in the reactant, steam reforming of methane was the dominant reaction, resulting in H_2/CO ratio close to 3. Using flue gas from combustion as TRM feedstock, it was found that H_2/CO ratio was enhanced using lower CH_4 amount in reactant. High-temperature flue gas was suggested for TRM for the activation requirement.

1. Introduction

CH_4–CO_2 reforming combines two of the most problematic greenhouse gases to generate syngas for the synthesis of clean liquid fuels and valuable chemicals. This process is therefore a promising reaction for global warming control. However, this process requires high energy input and there is a risk of carbon formation that would deactivate the catalyst [1]. To overcome these problems, a novel tri-reforming of methane (TRM) process that combines three generally used methane reforming reactions for syngas production was proposed by Song and Pan [2]. In TRM the following reactions are coupled and carried out in a single reactor:

Steam reforming of methane (SRM):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \Delta H^0_{298K} = +206\ \text{kJ/mole} \quad (1)$$

Dry reforming of methane with CO_2 (DRM):

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2, \Delta H^0_{298K} = +247\ \text{kJ/mole} \quad (2)$$

Partial oxidation of methane (POM):

$$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2, \Delta H^0_{298K} = -36\ \text{kJ/mole} \quad (3)$$

As shown in Eqs. (1)–(3) TRM combines the endothermic SRM and DRM reactions with the exothermic POM reaction. The heat released from POM is used as the heat supply for SRM and DRM and makes the TRM more energy efficient [3].

In addition to energy efficiency, TRM offers several advantages for syngas production compared with the single reaction described in Eqs. (1)–(3). As shown in Eq. (2), CO_2 is used as the feedstock for DRM. As noted by Song and Pan [2], the TRM concept does not require a pure CO_2 supply in the reaction. This implies that the flue gas from the combustion processes of power plants or the coke oven gas (COG) from iron-making industries can be used directly as a CO_2 source for TRM [4–6]. TRM can also be used to upgrade the syngas quality produced from biomass or coal gasification [7,8]. The H_2/CO ratio in syngas produced from tri-reforming can be adjusted using varied amounts of reactants to satisfy the requirement for further processes such as methanol and Fischer-Tropsch syntheses [9,10].

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Nomenclature

C_F	Forchheimer drag coefficient
c_p	gas specific heat, J kg^{-1} K^{-1}
D_{ij}	binary molecular diffusion coefficient, m^2 s^{-1}
D_i^T	thermal diffusion coefficient of species i, m^2 s^{-1}
d_p	catalyst particle diameter, m
F	volumetric flow rate of gas mixture, m^3 s^{-1}
f	delay factor
h	heat transfer coefficient, W m^{-2} K^{-1}
K	catalyst bed permeability, m^{-2}
K_j	surface adsorption equilibrium constant of species j, Pa^{-1}
K_j^C	surface adsorption equilibrium constant of species j in combustion reaction, Pa^{-1}
$K_{eq,i}$	equilibrium constant of reaction i
k	rate constant of reaction i, mol $Pa^{0.5}kg_{cat}$ s^{-1}, or mol Pa kg_{cat} s^{-1}
L	length of reactor, m
m_{cat}	catalyst weight, g
M_j	molecular weight of species j, g mol^{-1}
m_j	mass fraction of species j
$\dot{n}_j$	molar flow rate of species j, mole s^{-1}
N_G	number of species in the gas mixture
p	pressure, Pa
Q	volumetric flow rate, m^3 s^{-1}
q_c	energy source term due to the chemical reaction, W m^{-3}
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
R_b	reactor radius, m
R_j	production/destruction rate of species j, kg m^{-3} s^{-1}
r_i	kinetic rate of reaction i, mol kg_{cat} s^{-1}
r	radial direction
T	temperature, K
$\vec{V}$	velocity, m s^{-1}
v_0	averaged inlet velocity, m s^{-1}
X	species conversion
Y	species yield
x_j	mole fraction of species j
z	axial direction

Greek symbols

ε	catalyst bed porosity
η	effectiveness factor
λ	thermal conductivity, W m^{-1} K^{-1}
μ	viscosity, kg m^{-1} s^{-1}
ν	Stoichiometric coefficient
ρ	density, kg m^{-3}

Subscript

in	inlet
m	gas mixture
out	outlet
R	reaction
ref	reference state
cat	catalyst

TRM has been studied both experimentally and analytically in the literature. In the experimental study of Majewski and Wood [11], a nickel-silica core-shell catalyst was applied for TRM in a fixed-bed reactor. The optimal composition was determined for TRM for syngas production appropriate for methanol synthesis. Using thermodynamic analysis based on the Gibbs energy minimization, Zhang et al. [12] found that high temperature and low pressure are favorable to achieve high H_2 production and CO_2 conversion. Excessive addition of H_2O, O_2, and CO_2 bring about lower H_2 yield and CO_2 conversion, while low concentrations of H_2O, O_2, and CO_2 resulted in more intense carbon formation. In the study of Arab Aboosadi et al. [13], TRM performance in terms of CH_4 conversion, H_2 yield and H_2/CO ratio was demonstrated in a fixed-bed reactor using a 1-D heterogeneous model. Optimized reactant composition was reported by considering H_2 yield as the objective function. A similar study was carried out by Khajeh et al. [14] in which TRM performance using fluidized-bed and fixed-bed reactors was compared. Based on the concept that heat generated by TRM can be used as a heat source, Farniaei et al. [15] developed a mathematical model to simulate a coupled TRM-DRM reactor. Their results showed that CH_4 conversion at the DRM and TRM output sides reached 63% and 93%, respectively. In the study of Cho et al. [16] a simulation model was developed for syngas production from TRM. The TRM reactor consisted of a homogeneous part where oxidation leads to a temperature increase required for the reforming reactions and a catalytic part where the reforming reactions take place. The developed model was used to optimize the reactor design parameters and operating conditions.

Similar to the CO/CO_2 hydrogenation reaction, a challenging problem for TRM is to find active and stable catalysts. The most popular catalysts for TRM are nickel supported by a wide range of different materials (Al_2O_3, ZrO_2, CeO_2, etc.). Another problem is deactivation of supported metal catalysts due to carbon formation [17]. Carbon formation fouls the metal surfaces, blocks the catalyst support pores and voids, causing catalyst support physical disintegration and may also promote undesirable side reactions [18,19]. Because the TRM is similar to the catalytic partial oxidation (CPO) of methane [20,21], catalysts developed for the CPO may also be applied to TRM as reviewed by Al-Sayari [22].

Although TRM has been studied extensively in the past, most of these studies focused on finding the optimum reactant composition for producing a suitable H_2/CO ratio for further use. Very few studies focused on a complete, systematic study of the effects due to operating conditions and reactant composition. A two-dimensional numerical model solving the coupled governing equations including gas flow, heat transfer and chemical reaction is established in this study and applied to a fixed-bed TRM reactor. TRM performance characterized by CH_4 conversion, H_2 yield, CO yield and H_2/CO ratio is investigated under various operating conditions and syngas compositions. As noted by Song and Pan [2], TRM is originally developed for converting CO_2 in flue gas into useful syngas. Another objective of this study is to identify the CH_4 amount effect on converting flue gas into useful syngas which was also little discussed in the literature.

2. Physical and mathematical models

2.1. Mathematical model

The tubular fixed-bed reactor used in this study is shown in Fig. 1. The reactor has a length of L and a radius of R_b. A reactant consisting of CH_4, O_2, H_2O, CO_2, and N_2 is introduced into the reactor from the reactor bottom. Note that N_2 serves as the balance inert gas in the reaction. The pressure, temperature and volumetric