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Modeling of intensified glycerol steam reforming in a heat-exchange integrated microchannel reactor

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ABSTRACT

The aim of this study is to investigate glycerol steam reforming in a heat exchange integrated microchannel reactor involving solid wall separated, rectangular-shaped, parallel reaction and heating channels by means of mathematical modeling techniques. Heat needed for endothermic glycerol steam reforming taking place in Co-Ni/Al_2O_3 coated channels is supplied by steam flowing in the adjacent channels separated by solid walls. Simultaneous catalytic reaction and heat exchange within the microchannel reactor are modeled by 2D Navier-Stokes equations which were solved by the finite volume method in ANSYS 16.0 platform to study the effects of operational parameters, namely molar inlet steam-to-carbon ratio (S/C) and temperature of the reactive mixture, inlet temperature and velocity of steam, flow configurations of the reactive mixture and steam, and of structural parameters, i.e. reactor wall material and thickness of the wall between the reaction and heating channels on temperature distribution and on glycerol conversion. The results show that increasing S/C from 1 to 6 promotes H_2 and CO_2 selectivity, having average values of 64.7% and 21.2%, respectively. The same effect, however, suppresses CO selectivity from 12.8% to 10.8% and resulted in CH_4 selectivity below 2.7%. Product distribution is found to be in alignment with those of experimental studies reported in the literature. Heating by steam has an obvious contribution to glycerol conversion, which is found to be 73.3% and 63.8% in the presence and absence of steam heating, respectively. Counter- and co-current flow of steam with respect to reactive mixture, however, do not lead to a notable difference in conversion. Increasing steam inlet temperature from 663 K to 783 K improved conversion by 10.0%, whereas changing steam inlet velocity from 2 to 8 m/s did not change reforming channel temperature significantly. Reactor performance is significantly affected by increasing feed temperature of the reactive mixture from 673 K to 773 K which improved conversion by 11.7%. Higher glycerol conversions are also obtained by using thicker separating walls and thermally conductive wall materials, both of which favor heat flux into the reforming channel. Changing the wall thickness from 4×10^{-4} m to 1.2×10^{-3} m elevates conversion by 1.3%. A similar response is noted upon using silicon carbide instead of AISI steel as the material of construction of the microchannel reactor. In general, selectivity towards H_2 is positively correlated with the degree of uniformity of reaction channel temperature, which is also found to dampen undesired CH_4 selectivity.

1. Introduction

Increasing environmental concerns about the conventional fossil fuels and their monotonically elevating cost of exploration and production have accelerated efforts towards finding renewable and widely available alternatives. Among several options, biodiesel is attracting interest as it is carbon neutral and can successfully mimic the crude-oil based diesel [1,2]. Production of biodiesel is conventionally carried out by transesterification of animal-based or vegetable oils with methanol (or ethanol). In this process, one mole of glycerol is produced for every three moles of biodiesel, corresponding to the presence of ca. 10% of glycerol by weight in the reaction mixture [1,2]. This stoichiometry, however, causes undesirably high supply of glycerol: it is predicted that there will be three megatons of glycerol production by 2020, whereas the amount of glycerol consumption in commercial applications is expected to remain below five hundred kilotons [3]. This issue calls for the need of efficient conversion of excess glycerol into value added products such as H_2, which is a key component employed in critical petroleum refining operations such as hydrocracking and hydrotreating, as well as in powering fuel cell systems [4]. Currently, 95% of the H_2 comes from nonrenewable resources based on fossil fuels such as natural gas and naphtha [5].

Steam reforming (SR) is the conventional technique for converting hydrocarbons into a H_2-rich mixture. The process involves reaction of

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Nomenclature

A	Pre-exponential factor, mol/m^2 s kPa$^{(\beta+\gamma)}$
A_{metal}	Metal surface area of the catalyst, m^2/kg$_{cat}$
C_2	Inertial resistance coefficient of the washcoat, 1/m
$c_{p,i}$	Heat capacity of species i, J/kg K
$c_{p,m}$	Heat capacity of gas mixture, J/kg K
$D_{eff,i,m}$	Effective diffusivity of species i in the mixture, m^2/s
D_{ij}	Binary diffusion coefficient, m^2/s
$D_{i,m}$	Diffusivity of species i in the mixture, m^2/s
$D_{K,i}$	Knudsen diffusion coefficient of species i, m^2/s
d_p	Catalyst particle diameter, m
d_{pore}	Average pore diameter, m
E_A	Activation energy, J/mol
$\vec{\mathbf{F}}$	Momentum source/sink term, kg/m^2 s^2
F_i	Molar flux of species i, mol/m^2 s
$\mathbf{I}$	3 × 3 identity matrix, –
$\vec{J_i}$	Diffusive mass flux of species i, kg/m^2 s
k_{cat}	Thermal conductivity of the catalytic washcoat layer, W/m K
$k_{eff,m}$	Effective thermal conductivity of gas mixture in the washcoat layer, W/m K
k_i	Thermal conductivity of species i, W/m K
k_m	Thermal conductivity of gas mixture, W/m K
k_w	Thermal conductivity of the solid wall, W/m K
L	Length of the unit cell, m
M_i	Molecular weight of species i, kg/mol
M_m	Average molecular weight of gas mixture, kg/mol
N_g	Number of gas-phase species
p_i	Partial pressure of species i, kPa
p	Total pressure, kPa
r_{rxn}	Rate of reaction (rxn = DEC, WGS or MET), mol/kg$_{cat}$ s
R	Gas constant (= 8.314 J/mol K)
R_i	Consumption/generation rate of species i, mol/kg$_{cat}$ s
S_{BET}	BET surface area of the catalyst, m^2/kg$_{cat}$
S_i	Selectivity towards species i, %
T	Temperature, K
$\vec{\mathbf{v}}$	Velocity vector, m/s
V_{pore}	Catalyst pore volume, m^3/kg$_{cat}$
x, y, z	Cartesian coordinates
y_i	Mole fraction of species i, –
Y_i	Mass fraction of species i, –

Greek letters

α	Permeability of the washcoat, m^2
β	Partial reaction order for glycerol, –
ΔH°	Standard enthalpy of reaction, kJ/mol
ΔH_{rxn}	Enthalpy of reaction (*rxn* = DEC, WGS or MET), kJ/mol
ε_{cat}	Porosity of the washcoat layer, –
Φ_{ij}	Dimensionless parameter for the mixture of i and j, –
γ	Partial reaction order for steam, –
μ_i	Viscosity of species i, kg/m s
μ_m	Average gas mixture viscosity, kg/m s
ρ_{cat}	Density of the catalytic washcoat, kg/m^3
ρ_m	Density of gas mixture, kg/m^3
υ_i	Unitary constant that indicates if i is consumed or produced, –
$(\Sigma\upsilon)_i$	Sum of the atomic diffusion volumes for species i, –
τ_{cat}	Catalyst tortuosity, –

Subscripts and superscripts

cat	Catalyst
eff	Effective
i, j	Species indices
in	Channel inlet
out	Channel outlet
rxn	Reaction
w	Solid wall phase

Acronyms

DEC	Glycerol decomposition reaction
MET	Methanation reaction
SR	Steam reforming
S/C	Steam-to-carbon molar ratio at the inlet
WGS	Water-gas shift reaction

the hydrocarbon molecule with steam at temperatures in excess of ~800 K over a packed-bed of catalyst. Glycerol SR (Reaction (1)) is a combination of its decomposition (DEC) (Reaction (2)) and water-gas shift (WGS) (Reaction (3)) [6]:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2, \quad \Delta H^\circ = 128 \text{ kJ/mol} \tag{1}$$

$$C_3H_8O_3 \rightarrow 3CO + 4H_2, \quad \Delta H^\circ = 251 \text{ kJ/mol} \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H^\circ = -41 \text{ kJ/mol} \tag{3}$$

In addition to SR, glycerol-to-H_2 conversion is possible by partial oxidation (POX) or by oxidative steam reforming (OSR) routes, which are represented by the overall Reactions (4) and (5), respectively [3]:

$$C_3H_8O_3 + (3/2)O_2 \rightarrow 3CO_2 + 4H_2, \quad \Delta H^\circ = -598 \text{ kJ/mol} \tag{4}$$

$$C_3H_8O_3 + (3/4)O_2 + (3/2)H_2O \rightarrow 3CO_2 + (11/2)H_2, \quad \Delta H^\circ = -240 \text{ kJ/mol} \tag{5}$$

Among the three options, SR offers the highest H_2 concentration in the product mixture and does not depend on the requirement of pure O_2 or enriched air, which are expensive to obtain from air. These advantages, however, come at the expense of continuous requirement of external heat supply needed to handle the endothermicity of SR. Majority of the studies in the literature about glycerol SR, which are reviewed in-depth by Lin [3], are focused on developing catalysts that can deliver elevated conversions at reduced temperatures (i.e. with less external heat supply) with minimal carbon formation. In this context, Ni, Co and noble metals such as Rh, Pt and Ru supported over alumina, ceria and zirconia are studied with the aim of exploring either the effect of metal or the support or their interaction on glycerol conversion and on product distribution [3,6–8]. These studies, however, are carried out by using catalysts in particulate form within packed-bed reactor geometry. In other words, the effect of reactor configuration, which affects the degree of distribution of external heat to the catalyst bed and its effective utilization, is not addressed in detail. Bobadilla et al. [9] compared the performances of structured (monolith-shaped) and conventional (powder type and spherical shaped) Ni-based catalysts in glycerol SR. They reported that the activity and selectivity did not change with the catalyst geometry, but the monolithic catalyst demonstrated much better stability with no coke formation. Sadykov et al. [10,11] studied the steam/autothermal reforming of several biofuels including glycerol over structured nanocomposite catalysts at contact times in the order of milliseconds and reported that the microchannel substrate manufactured from a heat-conducting material enabled near equilibrium yields of synthesis gas without any transport limitations. Liu et al. [12] investigated glycerol ATR over Pt- and Pt/Rh-based monolithic catalysts at gas hourly space velocities in the order of 10^4 h^{-1} and reported complete glycerol conversions with distribution

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