



Modeling and simulation of catalytic partial oxidation of methane to synthesis gas by using a plasma-assisted gliding arc reactor

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ABSTRACT

In the present study, a numerical investigation of the catalytic partial oxidation (CPO) of methane to synthesis gas (syngas) using a gliding arc (GlidArc) reactor is presented. A 2D heterogeneous plug-flow model with radial dispersion and no gradients inside the catalyst pellet are used, including the transport equations for the gas and solid phase and reaction rate equations. The governing equations of this model formed a set of stationary differential algebraic equations coupled with the non-linear algebraic equations, and were solved numerically using in-house MATLAB® code. Model results of CPO of methane were compared to previous experimental data with the GlidArc reactor found in the literature. A close match between the calculated and experimental results for temperature, reactant (CH₄ and O₂) conversion, H₂ and CO yields and species mole-fraction was obtained. The developed model was extended to predict and quantify the influence of the gas hour space velocity (GHSV) as well as determine the influence of the reactor energy density (RED), the O₂/CH₄ molar ratio and the O₂/N₂ molar ratio. The predicted behaviors for the species mole-fraction, reactants conversion, H₂ and CO yields and temperature along the length of the reactor have been analyzed.

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1. Introduction

Over the last few decades, natural gas, which consists of 80–90% methane, has become one of the most important fossil fuels. It has been widely consumed for a variety of purposes, such as heating, electricity generation and producing chemicals [1]. Synthesis gas (syngas) is an important feedstock for the production of synthetic automotive fuels and for a variety of chemicals, such as methanol and its derivatives [2]. After removal of CO, it also provides hydrogen for ammonia synthesis, hydrogenations and fuel cell applications [3]. Syngas (H₂ and CO) production processes are well established with technologies such as partial oxidation, steam reforming, autothermal reforming and dry reforming. Among them, the most promising technology for small-scale syngas production is catalytic partial oxidation (CPO) [3–9]. Exothermic methane oxidation occurs simultaneously with endothermic methane reforming. A direct coupling of the exothermic and endothermic reactions exists over the same catalyst and makes this process attractive from an energy efficiency and safety perspective [10]. Various catalysts used on different supports have been reported to be active for the CPO of methane. Most catalysts contain a group VIII metal (Rh, Pt, Ru, Ni) as the active component on an oxide support [11]. Ni catalysts with alumina support are preferred due to high cost and limited availability of noble metals [12].

The shortcomings of the conventional reformers include size, large investments, limitations on rapid response, extreme operating conditions that limit the lifetime of a reactor, heat management (during the front end of the catalyst bed as the methane undergoes total oxidation), safety and operability [13]. The alternative novel plasma reforming option could provide original responses to these drawbacks in terms of reactivity, compactness and efficiency. Plasma reforming is electrically assisted reforming of fuel in which electrical energy is dissipated directly in the process gas through a specific high-voltage discharge [14]. Depending on the energy, temperature and ionic density, plasma reactors are classified as thermal or non-thermal (cold). A thermal plasma in a local thermodynamic equilibrium has an electron temperature (> 10,000 K) in each small volume of plasma that is equal to the gas temperature, excluding the radiation temperature. In a nonthermal plasma, the electron temperature is not in the local thermodynamic equilibrium, and the electrons can reach a temperature of 10⁴ to 10⁵ K, while the temperature of the gas can be as low as room temperature (300 to 3000 K) [15,16]. The gliding arc (GlidArc) is an example of nonthermal plasma. In the GlidArc reactor, an electric arc occurs between two or more diverging electrodes placed in a high-velocity gas flow. In such non-equilibrium plasma, gaseous species are chemically excited, dissociated or activated directly by electron impact. It is widely used for the modification of surface oxides, for the preparation and regeneration of catalysts and for catalytic synthesis and decomposition. A synergistic effect may be obtained through the combination of non-thermal plasma with a desirable catalyst. This catalysis–plasma process simultaneously has

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Nomenclature

Latin letters

C_p	specific heat ($\text{J.kg}^{-1}.\text{K}^{-1}$)
D_{er}	effective radial mass diffusion coefficient ($\text{m}^2.\text{s}^{-1}$)
D_j	diffusivity of the “j” species ($\text{m}^2.\text{s}^{-1}$)
d_p	average particle diameter of the catalyst (m)
f	friction factor
$GHSV$	gas hour space velocity ($\text{NL.g}_{\text{cat}}^{-1}.\text{h}^{-1}$)
h_p	heat transfer coefficient at the catalyst particle ($\text{W.m}^{-2}.\text{K}^{-1}$)
k_j	mass transfer coefficient of the “j” species (m.s^{-1})
M_j	molecular weight of the “j” species (kg.kmol^{-1})
P	pressure (bar or Pa)
R	universal gas constant: 8.314×10^3 ($\text{J.kmol}^{-1}.\text{K}^{-1}$)
r	radial position (m)
r_j	rate of consumption or formation of the “j” species ($\text{kmol.kg}_{\text{cat}}^{-1}.\text{s}^{-1}$)
r_p	average particle radius of the catalyst (m)
T	temperature (K)
u_z	superficial velocity of the fluid in the axial direction (m.s^{-1})
v	diffusion volume
w_j	mass fraction of the “j” species
y_j	molar fraction of the “j” species in the pseudo-phase
z	axial position in the tube (m)

Greek letters

ΔH_i	heat of the “i”th reaction (J.kmol^{-1})
ε	void fraction of the catalyst bed
λ	thermal conductivity ($\text{W.m}^{-1}.\text{K}^{-1}$)
μ	fluid viscosity (Pa.s)
ρ	density (kg.m^{-3})

Superscript and subscript

b	bulk
cat	catalyst
er	effective radial parameter
g	gas
i	the “i”th reaction
j	species “j”
p	particle

the advantage of high selectivity for the product from the thermal catalysis and fast startup from the plasma technique [17].

Even though the CPO reactor has been investigated over the past few decades [4,18–20], further scientific investigations are required to answer remaining open questions. Although methane oxidation is the simplest among the hydrocarbon oxidation processes but its kinetics is extremely complex because both exothermic and endothermic reactions are involved. In this process mass and energy balances are deeply coupled hence, the temperature variation does not translate directly to a reactant conversion. Therefore, CPO is a challenging and fascinating application where chemistry and transport phenomena are intrinsically connected with each other, determining the final product distribution. Appropriate, reliable and physically and chemically consistent mathematical models are required for understanding the complexity of the process and for further optimization and reactor control [21]. The species reaction rates are very fast for the CPO system, and at relatively long residence times, the kinetics slow down and the exit composition approaches equilibrium, which are dependent on temperature. The authors showed [22] that with the above approach, the model correctly describes the exit composition with the correct exit temperature, even if the onset of the

calculated profiles diverges greatly from the experimental data at the inlet of the catalyst [21].

Several modeling studies of the CPO of methane to syngas are available in the literature. De Groote and Froment [3] studied the 1D steady-state pseudo-homogeneous model of an adiabatic packed-bed reactor using Ni/Pt catalyst kinetics. Barrio et al. [23] investigated CPO reactions of methane in the presence of steam over a noble metal catalyst. A quasi-homogeneous 1D model was developed to model a lab-scale fixed-bed reactor to produce syngas. These model calculations can contribute to the optimization of the process with respect to the formation of important hot spots. de Smet et al. [12], Avci et al. [24], Nogare et al. [21] and Dalle Nogare et al. [22] studied the CPO of methane using 1D and/or 2D heterogeneous models. These models covered all aspects of major chemical kinetics and heat and mass transfer phenomena in the reactor. Trimm and Lam [25] studied autothermal reforming of methane on a Pt/Al₂O₃ catalyst. Lin et al. [26] developed kinetic models to simulate the catalytic autothermal reforming. Hoang and Chan [27] developed a 2D unsteady modeling of catalytic autothermal reforming of methane. Lattner and Harold [28] evaluated several reactor types for autothermal reforming of hydrocarbon fuels for the production of hydrogen in proton exchange membrane fuel cell systems. Chan and Ding [29] improved a previous 2D kinetic model by including the diffusion of gas species into the catalysts, non-plug flow gas velocity profile and non-uniform catalyst porosity in the reformer. Vesper and Frauhammer [9] discussed the modeling studies of the monolith reactor with a transient-state 2D two-phase dispersion model of a Pt monolithic reactor. Deutschmann and Schmidt [30] studied the steady-state 2D detailed-flow model of a monolithic channel using detailed kinetics of partial oxidation of a noble catalyst. Bizzi et al. [7,31,32] studied the partial oxidation of methane in a short contact-time, packed-bed reactor using a noble catalyst with and without detailed chemistry. Detailed chemistry may be required to discriminate different reaction mechanisms/steps, whereas global kinetics is sufficient for the reactor studies, such as scale up and design [5]. Most of the above mentioned investigations were carried out for packed-bed reactors, membrane fuel cell systems and monoliths. None of these studies included the effect of plasma on CPO reactors using a 2D heterogeneous model.

The aim of this study was to propose a 2D heterogeneous model for a CPO GlidArc reactor using intrinsic kinetics of a Ni-based catalyst. The model was validated with the previously reported, experimentally measured temperature profiles, together with data collected at the reactor exit reported elsewhere [33]. Finally, parametric sensitivity analysis with detailed numerical simulations was performed to determine the effect of various parameters and to develop a good understanding of the behavior of the CPO GlidArc reactor system.

2. Materials and methods

2.1. Experimental data

The experimental setup comprising the CPO GlidArc reactor and catalysts and the operating conditions to measure the exit species concentration and axial temperature profiles were presented in detail elsewhere [33]. Briefly, the data set used for this work contained the temperature profiles at a steady state and the exit concentration of the dry gas species. The temperature was measured with a moveable thermocouple in a thin, hollow pipe in the reaction chamber at three different places: in the plasma zone (T_p); at the maximum temperature in the catalytic bed zone (T_{max}); and at the exit temperature in the catalytic bed zone (T_{exit}). The product gasses were analyzed off-line using a commercial residual gas analyzer (RGA) combined with a gas chromatograph (GC). The product gasses from the exhaust pipe were obtained with a special gas syringe and then injected

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