Chemical Engineering Journal 238 (2014) 100–110

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Simulation of the methane conversion by partial oxidation in a porous medium reactor

S.S. Kostenko [*], A.N. Ivanova, A.A. Karnaukh, E.V. Polianczyk

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 Academician Semenov Ave., Chernogolovka 142432, Russia

HIGHLIGHTS

- We simulate the methane–oxygen–steam reforming in a filtration combustion reactor.
- A detailed kinetic mechanism of methane oxidation with soot formation is suggested.
- Combustion-wave temperature for rich methane–oxygen mixtures is lower than 1500 K.
- The steam-soot reaction reduces soot formation and increases hydrogen production.

ARTICLE INFO

Article history:
Available online 12 September 2013

Keywords:
Filtration combustion
Methane conversion
Reactor
Kinetics
Simulation

ABSTRACT

The methane/oxygen/steam mixture conversion in a porous medium reactor is investigated numerically. The two-temperature (gas/solid) one-dimensional model is employed. The model of the kinetics includes a set of gas-phase radical-chain reactions supplemented with the loss of radicals on the surface of inert solid, formation of soot and reactions of the latter with oxygen, water, and carbon dioxide. The computational experiment showed that the traveling (superadiabatic) reaction front establishes within the reactor. However, in contrast to predictions of thermodynamic models, owing to short residence time at a high temperature, the steam conversion reaction does not develop under the conditions studied.

1. Introduction

Conversion of natural gas to synthesis gases is extensively used in industry. Usually, conversion processes are carried out at high temperature. This implies energy expenditure not only for the endothermic stages of the methane conversion, but also for heating the reaction mixture. Use of catalysts allows one to reduce the process temperature, but it brings about the problems of catalyst poisoning and coking; still the processes are extremely energy consuming [1]. A possible approach to optimization of the methane conversion into synthesis gas via partial oxidation is to perform the process in the filtration combustion mode under superadiabatic conditions [2]. Filtration combustion (FC) is an exothermic process, which proceeds in two-phase systems under the conditions where a reactive gas filters through a porous solid material [3,4]. In this case, the energy expenditure is related to overall heat effect of the oxidation reaction. The oxygen consumption should also be minimized, as the energy expenditure for the oxygen production should also be taken into account. The conditions for superadiabatic heating in FC can be achieved in a reaction zone traveling concurrently with the gas flow over the porous matrix when, owing to the interphase heat exchange, the inherent heat recuperation occurs, and both porous medium and the gaseous products leave the hot reaction zone at a temperature substantially lower than the reaction temperature.

A number of studies were devoted to experimental investigations and numerical modeling of the methane conversion by partial oxidation with air in FC reactors [5], particularly, in the reverse flow FC reactor [6]. The kinetic modeling in these works involved detailed mechanisms of the gas-phase reactions, described in standard kinetic databases such as CHEMKIN and GRI [7–10]. The cited works showed that conversion of methane by partial oxidation could be performed in the superadiabatic mode, i.e., with enhanced energy efficiency.

A further improvement in the energy efficiency of the methane conversion might be achieved if oxygen in the conversion process were partially replaced with water. In this case overall heat effect of the process would be lower and the hydrogen yield higher due to the endothermic reactions of water with methane, which also yield hydrogen. The possibility to further enhance energy efficiency of methane conversion by addition of water to the reaction mixture could be materialized if the high temperature of the reaction zone were supported by the interphase

---

[*] Corresponding author. Tel.: +7 926 5981755.
E-mail address: kostsv@icp.ac.ru (S.S. Kostenko).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.09.012

Nomenclature

A	pre-exponential factor
c_i	specific heat for the ith component of the gas (J/(mol K))
c_s	specific heat for the porous medium (J/(kg K))
d_{eff}	effective pore size (m)
D_i	the diffusion coefficient of the ith component (m^2/s)
E	activation energy (J/mol)
F	heat capacity of the gas flow $F = v_g\sum_i c_i\rho_i$ (J/(m^2 s K))
G_i	flow rate of the ith gaseous component (mol/(m^2 s))
k_j, k_0, $k_{j\infty}$	rate constants
L	reactor length (m)
L_0	length of the initial hot step in the reactor (m)
n	order of the temperature dependence in the kinetic constant
p	pressure (Pa)
$[M]$	total concentration of all gaseous components (mol/m^3)
Q_j	enthalpy of the jth reaction ($Q_j = -\sum(\beta_{ij} - \alpha_{ij})\Delta h_i$) (J/mol)
R	gas constant (J/(mol K))
t	time (s)
T_g	temperature of the gas (K)
T_s	temperature of the porous medium (K)
T_s^0	initial temperature of the preheated porous medium (K)
v_g	gas flow velocity (m/s)
W_j	volumetric rate of the jth reaction (mol/(s m^3))
x	spatial coordinate along the reactor axis (m)
α_{ij}, β_{ij}	stoichiometric coefficients
Δh_i	enthalpy of formation of the ith component (J/mol)
ε	porosity
λ_g	thermal conductivity of the gas (J/(m s K))
λ_s	thermal conductivity of the porous medium (J/(m s K))
ρ_i	molar concentration of the ith gaseous component (mol/m^3)
ρ_s	density of the solid (kg/m^3)
φ	volumetric heat exchange coefficient (W/(m^3 K))

Subscripts

s	solid
g	gas
i	species number
j	reaction number
z	carbon
0	initial value

Superscript

0	reference value

heat recuperation. Earlier [11] we investigated conversion of the methane/oxygen/steam mixtures in a regime of superadiabatic filtration combustion. In this regime, the reaction zone of gas conversion propagates as a traveling wave in an inert porous medium. The attainment of the thermodynamically equilibrium composition of reaction products was assumed in [11]. Thermodynamic calculations for methane/oxygen/steam mixtures at high temperatures were made. On the basis of these calculations, we preliminary estimated the domain of the compositions for the reaction mixtures, which provide a possibility to combine a high yield of the desired products (CO and H_2) with a small net heat release. For these gas mixtures, the ignition conditions were investigated using the method previously developed in [12]. The apparent Arrhenius kinetic parameters of ignition for the simplified kinetic model were used as a closure for the equation set that described the running FC wave. An analytical solution in the limit of high inlet velocity of the gas mixture was obtained. This solution showed that the temperature in the combustion wave and methane conversion are governed by the kinetics of the initial stages of methane oxidation and by the overall heat effect of the gross reaction. Thus, it was shown that in the limit of high inlet velocity of the gas one might anticipate the combustion front propagation through the porous medium in the regime of a traveling wave with superadiabatic heating. However, a more detailed study of the process involving a detailed kinetic scheme is necessary, to check whether the assumptions made in the simplified model hold under practical conditions.

The kinetic modeling for the air–steam conversion of methane performed in [9,10] showed that the two stages in the conversion reaction are distinctively separated in time and space. The first stage is that of a partial oxidation of methane. On the first stage, the heat is released and water is formed. On the second stage, the water reacts with the residual methane, hydrogen and carbon monoxide being formed. The kinetic model used in these studies, however, did not take into account the heterophase reactions of active species, which unavoidably proceed in porous media.

In this work we continue the research of the methane partial oxidation in a porous medium reactor with admixing steam using a model, which also takes into account the heterophase reactions.

In the first part of this work we describe and test a kinetic model for a methane/oxygen/steam mixture in order to determine how the composition of the final products depends on the gas mixture composition and on the temperature. The estimates of the characteristic time during which the concentrations of gaseous products reached their thermodynamic values are made.

In the second part of this paper we report the results of numerical simulations based on this kinetic model for the propagation of a combustion wave in the porous medium reactor. The time dependent spatial distributions for the temperature in gas and solid, concentrations, and gas velocity were calculated for varied compositions of the reaction mixture and initial conditions. The calculations provide an estimate for the possible effect of water vapor added to the reaction mixture on the combustion wave propagation and on the formation of desired products.

2. Mathematical model

We consider the combustion of methane/oxygen/steam mixtures using a model substantially similar to the two-temperature model used in [13]. The model includes energy balance equations for the porous solid and the gas without heat loss to the environment. The inert porous solid and the gas are considered as interpenetrating continuous media, each one characterized by its own temperature; the media being coupled through a convective heat transfer coefficient. The equation set further includes the equation of state for the gas and the species balance equations. The choice of the reactive species and the reactions, which are included into the kinetic scheme describing the methane oxidation, is discussed further. Note here, that we consider not only gaseous species but also carbon deposits, which can be formed owing to the reactions of gaseous species with the solid surface. The model is one-dimensional. Thus, it describes the process in a perfectly heat-insulated tube filled with an inert porous medium (schematically shown in