



Conversion of methane to synthesis gas in a non-premixed reversed-flow porous bed reactor: A kinetic modeling

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ABSTRACT

The methane conversion to syngas by air-steam partial oxidation in a non-premixed reversed-flow porous bed reactor is investigated numerically. The calculations were performed using the two-temperature (gas/solid) one-dimensional model. The kinetic model incorporates a set of gas-phase radical-chain reactions, the radicals loss on the surface of inert solid, the formation of carbon deposits and the reactions of the latter with oxygen, water, and carbon dioxide. The results of the computational experiments were compared to the predictions of thermodynamic model. It was shown that the combustion temperature exceeds that predicted in thermodynamic model, while the concentrations of acetylene and unreacted methane in the products substantially exceed those predicted. A comparison of the conversion in a non-premixed reversed-flow reactor with that for premixed gas mixture in the regime of superadiabatic traveling wave shows that a higher combustion temperature is attained in the non-premixed case.

1. Introduction

The conversion of various hydrocarbon gases into a synthesis gas involves reforming process. This multimillion ton industrial process is a material- and energy-consuming one and any improvement in it will be welcome. Apparently, the lower is oxidant (oxygen, possibly in air) consumption in the process, the higher is its thermal efficiency and the yield of desired products (hydrogen and carbon monoxide). Note that, e.g., steam reforming with an external heating, which seemingly has zero oxygen consumption, still obeys this rule of thumb, once we take into account the oxygen (and mineral fuel) consumption elsewhere, where heating energy is generated.

The non-catalytic partial oxidation processes carried out in the superadiabatic regimes in inert porous matrix are attractive for hydrocarbons reforming into synthesis gas. The [nick]name *superadiabatic* refers to the reaction temperature in such a process substantially exceeding the adiabatic temperature of reaction (which by definition is the temperature that would be attained by the reaction products due to reaction enthalpy change¹ in adiabatic conditions). In these processes a considerable heat recuperation is achieved via the gas-solid heat exchange. This allows one to attain a high reaction temperature for a relatively low net heat release, i.e., for low energy expenditure of the process. In particular, such processes promise a possibility to enhance energy efficiency of conversion and to achieve the process

intensification. Another important feature, which the use of inert porous matrix also promises, is elimination of susceptibility of a catalyst to coking and poisoning, as the process relies not on the catalytic activity of the porous matrix but on the high reaction temperature.

The partial oxidation processes performed in superadiabatic regimes in porous media have been studied extensively. A comprehensive review of the state of the art is given in [1].

Important advantages of the approach stem from that, in the superadiabatic processes, the reactants lend the heat from the reaction products and thus one achieves a possibility to decouple the reaction temperature from the net heat effect of the process. Therefore, one might construe a process with a low net heat effect, while achieving the process intensification not by the application of a catalyst but by performing the reaction at a high temperature. Ideally, this process temperature should be limited only by the structural strength of the porous matrix and of the reactor vessel, because the higher temperature shifts the chemical equilibria in the favorable direction, i.e., to the formation of hydrogen and of carbon monoxide. The high temperature also accelerates the chemical reactions and thus provides the intensification of the process in the reforming reactor. At the same time, this high temperature must be achieved for the lowest possible energy cost, which in our case of partial oxidation is the net heat release from the chemical reactions occurring in the reactor.

Addition of water (steam) to the reaction system promises further

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¹ Actual composition of products and gross enthalpy change for a complex reaction.

Nomenclature

| | |
|---------------------------|---|
| A_j | Preexponential factor ($\text{m}^3/\text{mol}/\text{s}$) |
| c_i | Specific heat for the i -th component of the gas ($\text{J}/(\text{mol K})$) |
| c_s | Specific heat for the porous medium ($\text{J}/(\text{mol K})$) |
| D_i | the diffusion coefficient of the i -th component (m^2/s) |
| d_{eff} | Effective pore size (m) |
| E | Activation energy (J/mol) |
| F | Heat capacity of the gas flow $F = v_g \sum_i c_i \rho_i$ ($\text{J}/(\text{m}^2 \text{ s K})$) |
| G_i | Flow rate of the i -th gaseous component ($\text{mol}/(\text{m}^2 \text{ s})$) |
| k | Kinetic rate constant ($\text{m}^3/\text{mol}/\text{s}$) |
| L | Reactor length (m) |
| n | Order of the temperature dependence in the kinetic constant |
| p | Pressure (Pa) |
| T_s | Temperature of the porous medium (K) |
| T_g | Temperature of the gas (K) |
| t | Time (s) |
| v_g | Gas flow velocity (m/s) |
| W_j | Rate of the j -th reaction ($\text{mol}/(\text{s m}^3)$) |
| x | Spatial coordinate along the reactor axis (m) |
| α | Heat exchange coefficient ($\text{W}/(\text{m}^2 \text{ K})$) |
| α_{ij}, β_{ij} | Stoichiometric coefficients |

| | |
|----------------|---|
| ΔH_j | Enthalpy of the j -th reaction ($\Delta H_j = - \sum (\beta_{ij} - \alpha_{ij}) \Delta H_i^0$) (J/mol) |
| ΔH_i^0 | Enthalpy of formation of the i -th component (J/mol) |
| ε | Porosity |
| λ_s | Thermal conductivity of the porous medium ($\text{J}/(\text{m s K})$) |
| λ_g | Thermal conductivity of the gas ($\text{J}/(\text{m s K})$) |
| ρ_i | Molar concentration of the i -th gaseous component (mol/m^3) |
| ρ_z | Molar concentration of carbon (mol/m^3) |
| ψ_i | Molar fraction of i -th gas component in the mixture |

Subscripts

| | |
|-----|-----------------|
| i | Species number |
| j | Reaction number |
| g | Gas |
| s | Solid |
| z | Carbon |

Superscript

| | |
|---|-----------------|
| 0 | Reference value |
|---|-----------------|

enhancement of hydrogen yield for lower energy expenditure as the water might partially substitute oxygen as a reactant to yield additional hydrogen in endothermic reactions of steam methane conversion. Several studies were devoted to a search of possible further improvements in the partial oxidation processes by incorporating steam in the reforming process so as to reduce the oxygen consumption per unit methane and simultaneously increase the yield of hydrogen [2–4].

The experimental studies and modeling using detailed reaction kinetic mechanisms of filtration combustion of premixed ultra-rich methane-oxygen/air-steam in inert porous matrices show that despite the steam is added to the gas mixture it is rather produced than consumed in the process. This is due to the fact that the self-consistent temperature of filtration combustion “chooses” for itself a value too low to cause the non-catalytic reactions of water with methane with any noticeable rate [2–4]. The propagation velocity of the combustion wave through the porous bed is self-consistent with the combustion temperature and the latter for a sufficiently high gas supply rate is controlled by the kinetics of methane ignition [5].

Since the desired high temperature is not attained in the filtration combustion of premixed gases as a result of the reactive mixture prematurely starting to actively react, a novel version of a reciprocal flow reactor was proposed in [6,7]. The basic idea of the process is to achieve a higher reaction temperature by postponing mixing of the reactants until a high preheating is attained. Initially one of them

having a higher heat capacity gets highly preheated via heat exchange with the porous matrix and the mixing is performed further.

The scheme of the process is presented in Fig. 1.

The established cyclic process in the case of air-steam partial oxidation reforming operates as follows. During the first half-cycle, reactant A, air-steam mixture, is supplied to the reactor 1 via the three-way valve 6 from inlet 4. As the air filters through the porous matrix 2, which was preheated during previous half-cycle, it heats up and reaches the middle part of the reactor at a high temperature, while the part of the porous matrix adjacent to inlet 4 cools down. The reactant B (methane) is supplied via inlet 8 to the middle part of the reactor. The supply rates of air and methane are controlled so as to perform partial methane oxidation. Preheated oxygen reacts with methane releasing a substantial heat, which is partially consumed by parallel endothermic reactions. The reaction zone in the middle part of the reactor is narrow compared to the dimensions of the reactor. The hot syngas from the reaction zone filters through the porous matrix, which was cooled down near the outlet 3 during the previous half-cycle, and lends its sensible heat to the porous matrix. Thus, the syngas G leaves the reactor via outlet 3 and via valve 7 to withdrawal 9 being substantially cooled. When the porous matrix heats up to outlet 3, valves 6 and 7 are switched to reverse the direction of the gas flow within the reactor and the operation of the reactor during the second half-cycle proceeds in the mirrored way as compared to that in the first half.

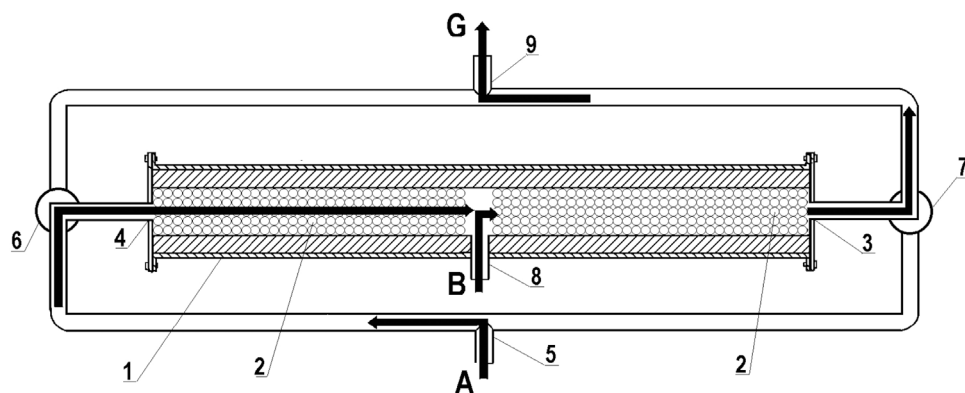


Fig. 1. Schematic of the process [6,7]. An odd half-cycle; 1 is the reactor vessel, 2 – inert porous matrix; 3, 4 – inlets/outlets of the reactor; 5 – supply of air-steam mixture A; 6,7 – three-way valves; 8 – supply of methane (reactant B); 9 – withdrawal of syngas G.

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