

Catalytic Combustion of Biogas-Hydrogen Mixtures in a Packed Bed Reactor

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Abstract

Catalytic combustion of lean premixed mixtures of biogas/air and biogas/hydrogen/air on Pt in a packed bed reactor has been investigated using detailed surface chemistry. Non-equilibrium, adiabatic and one dimensional flow assumptions have been adopted for simulation of the reactor. The interaction between two phases of porous medium is incorporated into the model via heat and mass transfer factors. Radiation heat transfer has been taken into account using effective thermal conductivity. All thermo-physical properties of the gas phase are considered to be temperature and concentration dependent. Two energy equations for two phases of the porous medium along with species transport equations are solved in the model. A mechanism of multi-step surface reactions, suitable for oxidation of lean mixture of methane/air, has been adopted from literature and employed for simulations. This mechanism includes 36 single step reactions with 11 surface and 6 gas phase species. Simulations have been conducted for oxidation of different biogas/air mixtures for the inlet temperature range of 700K to 900K at atmospheric pressure. The effect of the addition of hydrogen to the biogas/air mixtures has also been investigated. It is shown that hydrogen improves oxidation of methane.

Keywords: *Biogas, Catalytic, Hydrogen, Detailed Chemistry*

1- Introduction

The use of catalytic systems for the oxidation of common hydrocarbon fuels has been of crucial interest in recent decades. This technology makes it possible to achieve a complete combustion of very lean fuel-air mixtures at lower flame temperatures in combustion devices [1]. The complete combustion of such a mixture of fuels at lower temperature also results in lower NOx

emission. And this fact has made the catalytic combustion of lean fuel-air mixture an environmental approach to combust fossil fuels. Moreover, this technology enables the utilization of low heating value fuels such as biogas and landfill gas, considered as waste gases, and thus makes an additional source of energy. The catalytic oxidation of lean methane-air mixtures demonstrates a high level of efficiency at a cost which is

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competitive to other available technologies (e.g. thermal incineration) [2]. Methane is a major component of biogas and landfill gas and has a greenhouse effect up to 23 times worse than that of carbon dioxide. Therefore oxidation of these gases also attenuates the greenhouse effect of gases released into the atmosphere [3]. Although methane is abundant in nature, it is very hard to react in the gas phase. Many attempts have been made to improve the oxidation rate of methane in air. Much experimental and analytical evidence have reported that hydrogen can be an effective additive to methane, permitting faster combustion rates and the employment of leaner mixtures in gas-phase reactive combustion systems [4,5]. Also, it has been shown that catalytic oxidation of hydrogen can occur at very low temperatures (300K) for platinum [6-8]. Therefore, since hydrogen is very reactive in the presence of catalysts it may also be used to improve the rate of catalytic oxidation of other gaseous fuels [7,9].

Intensive theoretical and experimental studies have been conducted to improve the performance, controllability and understanding of the catalytic systems. Because of the complexity of the physical and chemical phenomena involved and the intimate coupling between them, most of the existing theoretical models for catalytic reactors are not valid over a wide range of operational conditions, although these models are rather complicated. Most of the research was conducted with monolith type reactors. This type has received much attention for industrial applications and consequently for experimental and theoretical studies [3,10,11]. However, a packed bed reactor can

also be considered as one ideal alternative for several industrial applications where the pressure drop is not an issue [12,13]. This is because 1) in comparison to the other reactor types, this reactor type is capable of rendering a higher fuel conversion rate at high space velocities, 2) it has a high specific geometric surface area, 3) it has small thermal conductivity and therefore the catalyst reaches a lower temperature level, while the reactor performance is not compromised, 4) it has very high mechanical and thermal resistances, and 5) it can be easily manufactured and altered. In comparison to monolith there is much less information available for modeling packed bed reactors. The information even narrows when it is necessary to include detailed chemistry in simulations. Primarily simplified models of catalytic reactors benefited from one-step or rather simplified chemistry models to describe the surface reactions [13,14]. However, due to changes in rate limiting steps with temperature and composition in most catalytic oxidation systems, detailed surface reaction mechanism is essential to capture the underlying physics and develop predictive models for reactor simulations. Bizzi et al. incorporated detailed surface chemistry in a model for simulation of catalytic partial oxidation of methane on Rh in a fixed bed reactor [15]. They studied the effect of space velocity and CH_4/O_2 ratio on the selectivity of CO and H_2 and predicted an optimum ratio for CH_4/O_2 in which a reactor yields the maximum conversion of CH_4 . Determination of flow pattern inside the reactors is also another important factor influencing the accuracy of the model. The need for employing an adequate model for

predicting flow pattern increases because of computational limitations for solving flow in the pores of an unstructured porous medium [13,14,16]. Especially if heat and mass transfer and chemical reactions influence the flow pattern. Therefore, adequate heat and mass transfer coefficients must be employed to obtain the temperature and species concentration in the bulk of the flow and in the vicinity of the catalyst surface to calculate the reaction rates more accurately [16,17].

Treating either the structured or unstructured porous medium using the volume average method for energy calculations has been proved to produce erroneous temperature profile in the catalytic reactors, since the amount of heat released in one phase is much different from that of other phases, and also the thermophysical properties of the gas phase may differ drastically from that of the solid phase [18]. This simplification has also been proved to bring about incorrect prediction of ignition temperature [13]. Thus, two-phase treatment for the reactors often is adopted.

In this work oxidation of lean mixture of biogas (CH_4/CO_2) and biogas/hydrogen in a catalytic packed bed type has been simulated. Therefore, precautions have been taken in order to adopt an adequate mechanism for surface reactions and suitable models for heat and mass transfer. The set of governing equations of the model have been solved using the commercial software, FLUENT [19], along with a number of modifying subroutines.

2- Physical description of the problem

A premixed, preheated homogeneous fuel/air mixture enters into a cylindrical packed bed, initially at uniform temperature. The fuel and oxygen reach the catalyst available sites and are adsorbed, each covering its share of the catalyst surface. The adsorbed species reacts on the surface and the heat released from the reactions changes the temperature which in turn affects the reaction rates. A portion of the heat increases the solid temperatures and the rest is transferred to the gas phase. This process continues until a steady state condition for both phases is achieved. The heat received in the gas phase may be high enough to promote the reaction in this phase. Several modes of heat transfer contribute to the transport of the heat from the solid surface; convective heat transfer between the gaseous mixture and pellets, axial heat conduction and radiation between the pellets. Convection heat transfer provides a coupling between gas and solid phase temperatures. Moreover, the heat conduction redirects the heat from the downstream section of the bed to its upstream part. Also, radial heat transfer may exist in the reactor if there is heat loss from the reactor wall or non-uniformity in the flow in the radial direction. However, the present model does not include radial heat transfer in the whole reactor since the reactor is assumed to operate under adiabatic conditions and the fluid flow is uniform. This makes the problem simpler and provides a better opportunity for employing multi-step chemical kinetics. Fig. 1 shows a schematic diagram of the physical model under consideration for the packed bed.

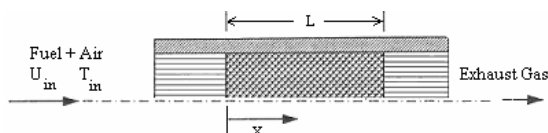


Figure 1. Schematic diagram of the packed bed

It is considered that gas and solid are not in local thermal equilibrium. Therefore, separate energy equations must be solved for each phase. Gaseous radiation is negligible compared to the surface radiation of the pellets. Thermophysical properties of the gas species are a function of the local temperature and concentration and the properties of the bed are uniform and temperature independent. Since the mixtures under study are lean, dilute approximation is adopted for the diffusion of species. Pressure is assumed to remain constant in the reactor since the reactor length is short and also space velocities are not very high.

3- Surface chemistry

Several surface reaction mechanisms have been proposed for partial or complete oxidation of methane on the surface of Pt. Hickman and Schmidt developed a mechanism comprising 19 elementary surface reactions for oxidation of methane on the surface of platinum [20]. The one-step dissociative adsorption of methane to C(s) and H(s) which appears in this mechanism seems to be rather non-realistic. However, they obtained good agreement with the experiment using the mechanism. Deutschmann et al. proposed a mechanism consisting of 23 elementary steps including a hierarchical dissociation of CH₄ to C(s) and H(s) via CH₃(s), CH₂(s) and CH(s) [9]. They also included the dependency of activation

energy, on catalyst surface coverage, for hydrogen and oxygen desorption from Pt surface. They used this mechanism to predict catalytic ignition of methane in a monolith reactor. Since pre-factors (i.e sticking and pre-exponential coefficient) and activation energies of elementary reactions are not independent of the coverage of the catalyst surface, there have been attempts to include this effect in recently proposed mechanisms. Zerkle et al. postulated a mechanism for partial oxidation of ethane on Pt [21]. The methane oxidation of this work was used by Quiceno et al. to propose a mechanism for partial oxidation of methane on Pt surface [22]. The steps in their mechanism are almost the same as those of Deutschmann's [9]. The dependence of pre-factors and activation energies on coverage of the catalyst surface has also been taken into account by Aghalayam et al. [23]. They derived a reaction mechanism for oxidation of methane, hydrogen and carbon monoxide on the surface of platinum. BUI-QEP method was used for optimization of the pre-factors and activation energies while taking thermodynamic consistency into account. Initial values for the pre-factors were taken from transition theory and those of activation energies were taken from literature. Most of the surface reaction mechanisms only include C1 surface species and eliminate C2 adsorbed hydrocarbons since there is no sufficient thermodynamic and kinetic information available about these species [21], [24]. Chou et al. proposed a C1 mechanism for oxidation of lean methane-air mixture [25]. They added one extra step to Deutschmann's mechanism to account for the dissociative adsorption of methane in the

presence of oxygen. This step is responsible for catalytic self ignition of methane in oxygen dominated coverage for catalyst surface. The surface reaction steps used in the present work comprises 36 reactions between 11 surface species (CH₃(s), CH₂(s), CH(s), C(s), CO(s), CO₂(s), H₂O(s), OH(s), H(s), O(s) and Pt(s)) and 6 gas phase species (CH₄, H₂, O₂, CO, CO₂ and H₂O). Reaction steps are chosen based on the steps which have been used in Deutschmann's [9], Aghalayam's [23] and Chou's [25] mechanisms, developed for the oxidation of lean air-methane mixtures at low and moderate temperatures (oxygen dominated surface coverage). Pre-factors and activation

energies for these steps have been taken from the work of Zerkle et al. [21] and Quiceno et al. [22]. A number of modifications for the reaction steps and kinetic coefficients have been performed in order to match the results of the mechanism with the available experimental data [6,7]. The use of coverage dependent pre-factors and activation energies for some of the reaction steps makes the mechanism suitable for a wider range of operating temperatures since the catalyst oxygen free and oxygen dominated regimes demand different activation energies for the reaction steps [23]. Table 1 illustrates the reaction steps and corresponding kinetic coefficients used for simulations.

Table 1. Surface Reaction Mechanism of Oxidation of Methane on Platinum.
Units: S₀ [-], A [S⁻¹], E_a [kJ/mol], μ [-], ε [kJ/mol]

	S ₀ or A	β	E _a	μ	ε	
<i>Adsorption Reactions</i>						
1	H ₂ + Pt(s)+ Pt(s) => H(s)+ H(s)	0.046	0.0	-1.0		H(s)
2	O ₂ + Pt(s)+ Pt(s) => O(s)+ O(s)	0.07 (300/T)	0.0			
3	CH ₄ + Pt(s)+ Pt(s) => CH ₃ (s)+ H(s)	0.0009	72.0			
4	CH ₄ + O(s)+ Pt(s) => CH ₃ (s)+ OH(s)	1.36E+10	0.7	42.0		-8.0
5	H ₂ O+ Pt(s) => H ₂ O(s)	0.75	0.0			
6	CO ₂ + Pt(s) => CO ₂ (s)	0.005	0.0			
7	CO+ Pt(s) => CO(s)	0.84	0.0			
8	H+ Pt(s) => H(s)	1.0	0.0			
9	O+ Pt(s) => O(s)	1.0	0.0			
10	OH+ Pt(s) => OH(s)	1.0	0.0			
<i>Desorption Reactions</i>						
11	H(s)+ H(s) => Pt(s)+ Pt(s)+ H ₂	1.0E13	64.4		10.0	H(s)
12	O(s)+ O(s) => Pt(s)+ Pt(s)+ O ₂	1.0E13	235.0		188.0	O(s)
13	H ₂ O(s) => H ₂ O+ Pt(s)	4.5E12	41.8			
14	CO ₂ (s) => CO ₂ + Pt(s)	1.0E13	27.1			
15	CO(s) => CO+ Pt(s)	1.0E15	146.0		33.0	CO(s)
16	H(s) => H+ Pt(s)	6.0E13	254.4		2.8	H(s)
17	O(s) => O+ Pt(s)	1.0E13	358.8		94.0	O(s)
18	OH(s) => OH+ Pt(s)	5.0E13	251.1		167.0	O(s)
<i>Surface Reactions</i>						
19	H(s)+ O(s) => OH(s)+ Pt(s)	3.5E12	11.2			
20	OH(s)+ Pt(s) => H(s)+ O(s)	2.0E12	77.3		73.2	O(s)
21	H(s)+ OH(s) => H ₂ O(s)+ Pt(s)	5.5E12	66.2			
22	H ₂ O(s)+ Pt(s) => H(s)+ OH(s)	3.1E10	101.4		-167.0	O(s)
23	OH(s)+ OH(s) => H ₂ O(s)+ O(s)	2.0E12	74.0			
24	H ₂ O(s)+ O(s) => OH(s)+ OH(s)	2.7E11	43.1		-240	O(s)
25	C(s)+ O(s) => CO(s)+ Pt(s)	1.0E11	0.0			
26	CO(s)+ Pt(s) => C(s)+ O(s)	1.0E11	236.5		33.0	CO(s)
27	CO(s)+ O(s) => CO ₂ (s)+ Pt(s)	1.0E11	117.6		33.0	CO(s)
28	CO ₂ (s)+ Pt(s) => CO(s)+ O(s)	1.0E11	173.3		-94.0	O(s)
29	CO(s)+ OH(s) => CO ₂ (s)+ H(s)	2.72E10	38.7		33.0	O(s)
30	CO ₂ (s)+ H(s) => CO(s)+ OH(s)	2.72E10	8.4			
31	CH ₃ (s)+ Pt(s) => CH ₂ (s)+ H(s)	3.4E13	70.3			
32	CH ₂ (s)+ H(s) => CH ₃ (s)+ Pt(s)	8.4E13	0.0		2.8	H(s)
33	CH ₂ (s)+ Pt(s) => CH(s)+ H(s)	2.0E14	58.9		-50.0	C(s)
34	CH(s)+ H(s) => CH ₂ (s)+ Pt(s)	8.4E13	0.0		2.8	H(s)
35	CH(s)+ Pt(s) => C(s)+ H(s)	8.4E13	0.0		2.8	H(s)
36	C(s)+ H(s) => CH(s)+ Pt(s)	3.4E13	138.0			

Since only lean mixtures of CH₄/Air at low and moderate temperatures were to be investigated, reaction R3 was included in the mechanism [25]. This reaction becomes important at the oxygen free region on the catalyst surface for dissociative adsorption of methane on platinum. In other words, it is responsible for the onset of methane oxidation on the surface and leads to activity of R2. All reactions are irreversible and the necessary thermodynamic properties for surface species (i.e. heat of adsorption and desorption) and heat released from surface reactions have been adopted from [26].

4- Model equations

The model comprises one dimensional transient equations of mass and energy conservation. These equations are described as follows:

Continuity equation

$$\frac{\partial \rho_g}{\partial t} + \frac{\partial(\rho_g u_g)}{\partial x} = 0 \quad (1)$$

Species mass balance in the gas phase

$$\rho_g \frac{\partial Y_{g,i}}{\partial t} + \rho_g u_g \frac{\partial Y_{g,i}}{\partial x} = -\rho_g D_{i,m} \frac{\partial^2 Y_{g,i}}{\partial x^2} + \frac{k_{m,i}}{\varepsilon} a_v \rho_g (Y_{s,i} - Y_{g,i}) + M_i \dot{R}_{g,i} \quad (2)$$

Species mass balance on the catalyst surface

$$k_{m,i} \rho_g (Y_{g,i} - Y_{s,i}) = M_i \dot{R}_{s,i} \quad (3)$$

Energy balance in the gas phase

$$\rho_g c_g \frac{\partial T_g}{\partial t} + \rho_g c_g u_g \frac{\partial T_g}{\partial x} = -k_g \frac{\partial^2 T_g}{\partial x^2} + \frac{h}{\varepsilon} a_v (T_s - T_g) + \sum_i M_i \dot{R}_{g,i} H_i \quad (4)$$

Energy balance for solid phase

$$\rho_s c_s \frac{\partial T_s}{\partial t} = -k_s \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial q_{rad}}{\partial x} + \frac{h}{1 - \varepsilon} a_v (T_g - T_s) + \sum_i \frac{a_v}{1 - \varepsilon} M_i \dot{R}_{s,i} H_i \quad (5)$$

Ideal gas law

$$pM_g = \rho_g RT_g \quad (6)$$

Since only the lean mixtures of fuel-air were considered, the diffusion coefficients, $D_{i,m}$, in the equations of species balance were obtained using dilute mixture assumption and kinetic theory. However, the diffusive mass transfer in the gas phase is not significant in the longitudinal direction, in comparison to the convective mass transfer in this direction [15]. This is because the Peclet number is high (> 500) for all the operating velocities. The conduction and radiation heat transfer in porous media in the longitudinal direction have been taken into account using effective thermal conductivity [27]. Adiabatic condition was adopted for the reactor walls since the experimental data were obtained for a well insulated reactor, including an extra heater for compensating the effect of possible heat losses [6,7].

Thermal interaction between the solid and gas was taken into account using convective heat transfer coefficient, h , which was obtained from heat transfer factor, J_H , as follows [17]

$$J_H = \frac{h}{\rho u c_p} \left(\frac{\mu c_p}{k_g} \right)^{2/3} \quad (7)$$

Where J_H is computed from

$$J_H = \begin{cases} 0.91 \text{Re}^{-0.51} \varphi, & 0.01 < \text{Re} < 50 \\ 0.61 \text{Re}^{-0.41} \varphi, & 50 < \text{Re} < 1000 \end{cases} \quad (8)$$

The mass transfer factor $k_{m,i}$ in the equations of species mass balance for gas phase and on the surface of the catalyst is computed in an analogous way to calculate the heat transfer coefficient, h . This is performed using the Chilton Colburn analogy [28]

$$J_D = \frac{k_{m,i}}{\rho v_x} \left(\frac{\mu}{\rho D_{m,i}} \right)^{2/3} \quad (9)$$

where

$$J_D = \begin{cases} 0.91 \text{Re}^{-0.51} \varphi, & 0.01 < \text{Re} < 50 \\ 0.61 \text{Re}^{-0.41} \varphi, & 50 < \text{Re} < 1000 \end{cases} \quad (10)$$

In equations 8 and 10 Re number is defined as

$$\text{Re} = \frac{\rho u_g}{a_v \varphi \mu} \quad (11)$$

where φ is the pellets shape factor and equals 1.0 for spherical pellets, 0.91 for cylindrical pellets and 0.81 for flakes [17]. In this work 0.91 was assigned to this parameter since cylindrical pellets were used in the simulations.

Boundary conditions

The following boundary conditions were employed for simulations,

$$\begin{aligned} \text{At } x = 0: \quad T_g &= T_{g,\text{inlet}}, \quad h(T_g - T_s) = -k_s \frac{\partial T_s}{\partial x}, \\ Y_g &= Y_{g,\text{inlet}} \end{aligned} \quad (12)$$

$$\text{At } x = L: \quad \frac{\partial T_g}{\partial x} = 0, \quad \frac{\partial T_s}{\partial x} = 0, \quad \frac{\partial Y_{g,i}}{\partial x} = 0 \quad (13)$$

The reactor wall was considered to be adiabatic, therefore there is no need to include heat transfer in the radial direction.

Surface chemistry equations

Chemical reactions on the catalyst surface appear in the form of a source term in the species balance equation for the surface and energy conservation equation of the solid phase (eq. 3 and 5). $\dot{R}_{s,i}$ is the rate of depletion or creation of species i on the surface. If a set of elementary reactions comprises N_s species and K_s elementary reactions are involved in the reaction mechanism, then one may write

$$\dot{R}_{s,i} = \sum_{k=1}^{K_s} \nu_{ik} k_{fk} \prod_{j=1}^{N_g+N_s} [X_j]^{v'_{jk}}, \quad (i=1, \dots, N_g + N_s) \quad (14)$$

in this equation $[X_j]$ is the molar concentration of species j on the surface and k_{fk} is the forward rate and is calculated from

$$k_{fk} = A_k T^{\beta_k} \exp(-E/RT) \prod_{i=1}^{N_s} \Theta_i^{\mu_{ik}} \exp(\varepsilon_{ik} \Theta_i / RT) \quad (15)$$

where ε_{ik} and μ_{ik} are coverage dependence parameters and Θ_i is the fraction of the catalyst surface covered by the adsorbed species i . Surface coverage of species i , Θ_i , and surface molar concentration of this

species $[X_i]$ relate via Γ , that is surface site density,

$$[X_i] = \Gamma \Theta_i \quad (16)$$

Γ is the number of moles of catalyst per unit area and depends on the lattice structure of the catalyst. The determination of evolution of surface species concentration requires a system of ODE

$$\frac{d\Theta_i}{dt} = \Gamma R_{s,i}, \quad (i = 1, \dots, N_s) \quad (17)$$

At present, contribution gas phase reaction effect is neglected since the reactor operates at atmospheric pressure and the residence time of the gas in the reactor is not more than 10 ms [9,14].

Numerical Scheme

Solving the governing equations (equations 1-6) for packed bed has been carried out using the commercial software FLUENT [19]. In order to introduce surface reaction rates, the corresponding heat release in the solid phase, and also to embed an extra energy equation for this phase of packed bed and species balance equation on the surface, a number of modifying subroutines have been developed and used. To improve the numerical accuracy of discretization of spatial and temporal derivatives, QUICK scheme and second order method have been used, respectively. The stiff nature of surface chemistry equations is due to a wide range of rates for different reaction steps. Therefore, a stiff system integrator is required to be employed for this purpose. The system of

ODE for surface reactions, equation 17, is treated by a coupled stiff solver. This alleviates the rigorous numerical stiffness of the chemistry system of equations which needs to be solved at each computational time step of flow. Moreover, proper initial estimates for coverage of the surface species can alleviate the stiffness of the ODE system in the very first stages of the solution. 800 computational cells have been used for one dimensional spatial discretization of the domain and a time step of 1×10^{-5} second have been used for simulations of the packed bed reactor.

5- Results and discussion

Reactors specifications

Simulations were conducted for the oxidation of a lean mixture of CH₄/Air, $\Phi=0.35$, in the packed bed reactor. In order to validate the model, experimental data from [6,7] have been used and all conditions and reactor properties have been considered to be the same. The fixed bed for which simulations were carried out has a length of 5 cm and a porosity of 0.4. The pellet density, specific heat and surface emissivity were respectively 100 kg/m³, 837 J/kg.K and 0.6. Thermal conductivity for Al₂O₃ was chosen to be temperature dependent according to [7]. The approach velocity of the homogeneous mixture for all simulations was 1.0 m/s at a reference temperature of 293K. This means that the physical inlet velocity increases as the inlet temperature rises; however the mass flow rate stays constant. Pressure along the reactor was assumed to remain constant and atmospheric, 89Kpa. The catalyst used was deposited polycrystalline Pt on Al₂O₃

substrate in the form of cylindrical pellets with both a length and diameter of 0.0032m. The reactor is embedded in a cylindrical quartz tube with an inside diameter of 0.028m.

Model validation

As mentioned before, the surface kinetic model employed was adopted from literature [9, 22, 24, 25]. The site density for the catalyst was assumed to be 2.72×10^{-9} mol/cm². Since there was no information about the specific surface geometry of the pellets, this parameter was chosen as a fitting parameter to minimize the deviation between the model and the experiment. It was concluded that the total specific surface geometry for active catalyst sites for a fixed bed reactor is 2.93. The comparison between the experiment and the computations for oxidation of CH₄ and H₂, both with equivalence ratios of 0.35, in the reactor is presented in Fig 2.

The developed reactor model has also been validated using single step global reaction for oxidation of CH₄, CO and H₂ and their mixtures on Pt and Cr₂O₃/Co₃O₄ as catalysts under the same operating conditions. The corresponding results are in good agreement with available experimental data [6].

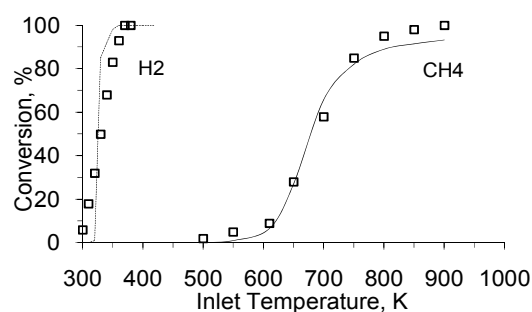


Figure 2. Comparison between experiment [6,7] and calculations performed with surface kinetic model presented in Table1. — calculations, □ experiment.

Combustion of Biogas in the packed bed reactor

Using this model, conversion of CH₄ in three different mixtures with CO₂ (CH₄ / CO₂: 2/3, 1/1 and 3/2), each with 3 different equivalence ratios (0.2, 0.3 and 0.4) has also been predicted. The corresponding compositions of the resulted mixtures have been presented in Table 2. Fig. 3 shows the predicted fuel conversion for the inlet temperatures ranging from 700K to 900K. It can be seen that for the same equivalence ratio the conversion of fuel remains almost constant when the amount of CO₂ is changed in the mixture. This is because CO₂ molar concentration of is less than 0.06 in all mixtures, therefore it has no pronounced effect on specific heat of the mixture.

Table 2. CH₄/CO₂/Air mixture composition

ϕ	CH ₄ / CO ₂ = 2/3				CH ₄ / CO ₂ = 1/1				CH ₄ / CO ₂ = 3/2			
	CH ₄	CO ₂	O ₂	N ₂	CH ₄	CO ₂	O ₂	N ₂	CH ₄	CO ₂	O ₂	N ₂
0.2	0.020	0.030	0.200	0.75	0.02	0.02	0.202	0.758	0.020	0.015	0.203	0.763
0.3	0.029	0.044	0.195	0.732	0.03	0.03	0.198	0.742	0.030	0.020	0.200	0.75
0.4	0.038	0.057	0.190	0.721	0.039	0.039	0.194	0.728	0.039	0.026	0.196	0.739

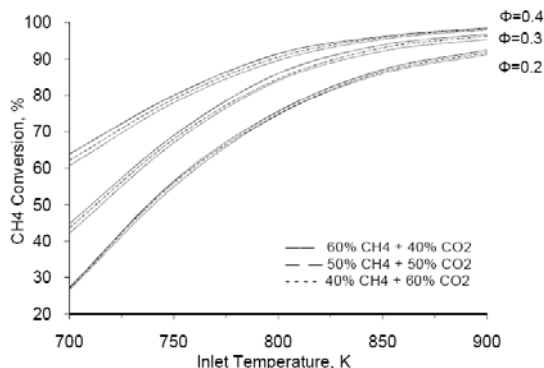


Figure 3. Conversion of CH_4 as a function of inlet temperature; for three ratios of CH_4/CO_2 in fuel composition with equivalence ratios of 0.2, 0.3 and 0.4

It should be mentioned that for catalytic oxidation of very lean mixtures of methane/air, the addition of diluents has no significant effect on the fuel conversion, provided that the concentration of fuel is kept constant and the mixture is still lean. It can be seen that concentration of methane influences the oxidation rate much more than the ratio of CH_4/CO_2 in the fuel mixture. This is why a zero order Arrhenius rate with respect to oxygen can be used for lean mixtures when a single step global reaction is adopted for a model [14]. Fig. 4 demonstrates

the effect of replacing air with CO_2 as a diluent when the concentration of CH_4 is kept constant and the mixture is still lean.

The effect of hydrogen addition on the oxidation of biogas in the reactor was also investigated using the model. Table 3 includes the concentration of fuel/ hydrogen/ air mixture considered for simulations. The concentration of hydrogen was kept identical, 0.01, for all mixtures and the equivalence ratio of the fuel was altered by changing the equivalence ratio. The corresponding results for the effect of hydrogen addition to the oxidation of CH_4 are presented in Fig. 5.

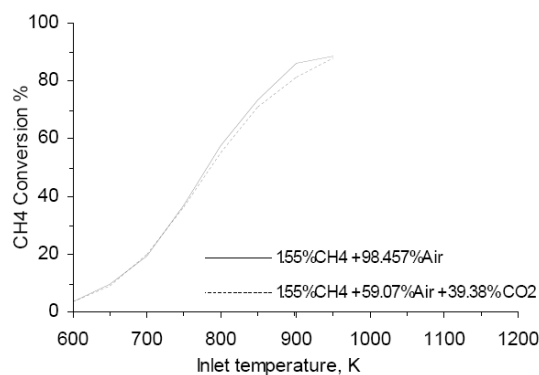


Figure 4. Effect of addition of diluent, CO_2 , on catalytic oxidation of methane in the reactor

Table 3. $\text{CH}_4/\text{CO}_2/\text{H}_2/\text{Air}$ mixture composition

ϕ	$\text{CH}_4 / \text{CO}_2 = 2/3$					$\text{CH}_4 / \text{CO}_2 = 1/1$					$\text{CH}_4 / \text{CO}_2 = 3/2$				
	CH4	CO2	H2	O2	N2	CH4	CO2	H2	O2	N2	CH4	CO2	H2	O2	N2
0.2	0.017	0.026	0.01	0.199	0.734	0.018	0.018	0.010	0.201	0.753	0.018	0.012	0.01	0.202	0.758
0.3	0.027	0.040	0.01	0.194	0.729	0.027	0.027	0.010	0.197	0.739	0.027	0.018	0.01	0.198	0.747
0.4	0.035	0.053	0.01	0.189	0.713	0.036	0.036	0.010	0.193	0.725	0.037	0.024	0.01	0.195	0.734

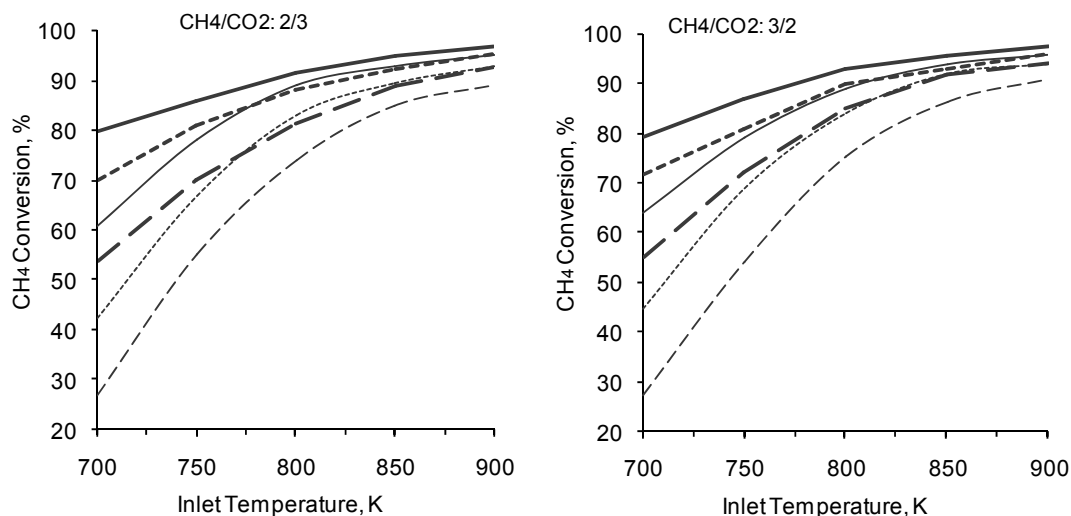


Figure 5. Methane conversion in the reactor as a function of inlet temperature
 — — $\Phi=0.2$, - - - $\Phi=0.3$ and — — $\Phi=0.4$, Thick lines show the
 conversion for the mixtures including 1% H_2

H_2 is oxidized completely at very low inlet temperatures (Fig. 2) and does not influence the process of CH_4 oxidation chemically since the mixtures are lean. Therefore, the role of hydrogen addition to the mixture is to release heat and increase temperature along the bed. From Fig. 5 it is perceived that hydrogen can improve the oxidation process of methane on the catalyst surface. This effect is more pronounced around light off temperature. The reason is that, around this temperature the sensitivity of CH_4 conversion to temperature is rather high. This is why hydrogen improves the oxidation of methane more significantly around this temperature. In this case, again the concentration of CH_4 in the mixture is an important factor and the conversion rate increases as the concentration of methane increases.

6- Conclusions

It was shown that the process of catalytic oxidation of methane and hydrogen in the packed bed reactor at initial temperatures of 700 - 900K can be predicted using detailed surface chemistry. The effect of diluent was proved to be less significant for lean conditions, provided that the concentration of fuel in the mixture is constant. Moreover, increasing the amount of methane in the mixture improves the reaction rate on the catalyst surface. However the conversion rate of methane for three different mixtures of CH_4 and CO_2 (CH_4/CO_2 : 2/3, 1/1 and 3/2) are very close at the same inlet temperatures and equivalence ratios. It was also shown that the oxidation of methane can be improved using a small amount of hydrogen in the fuel/air mixture for the same value of the mixture equivalence ratio.

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8- Nomenclature

Roman Symbols

β	temperature exponent
ε	porosity
ϕ	shape factor
Γ	surface site density, kmol/m ²
μ	viscosity, N.s/m ²
θ	surface coverage fraction
ρ	density, kg/m ³
ν	stoichiometric coefficient

Letters

H_i	enthalpy of species i , J/kg
j_H, j_D	convective heat & mass transfer factor
k	conduction heat transfer coefficient of gas, W/m K
k_f	forward Arrhenius rate
$k_{i,m}$	convective mass transfer coefficient of species i , 1/m ² s
K_g, K_s	number of steps in gas and surface
L	reactor length, m
\dot{R}_s	species production rate on surface, kmol/m ² s
t	time, sec
T	temperature, K
u_g	velocity, m/s
x	x coordinate, m
M_i	molar mass of species i . kg/kmol
N_g, N_s	number of gas and surface species

p	pressure, Pa
q_{rad}	Radiative heat flux, W/m ²
R	universal gas constant, kJ/kg.K
\dot{R}_g	species production rate in gas phase, kmol/m ³ s
X	molar concentration, kmol/m ³
Y_i	mass fraction of species i

Subscript

eff	effective
i, j, k	index
g	gas phase
s	surface, solid

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