UDC 536.46

METHANE-TO-HYDROGEN CONVERSION IN A REVERSIBLE FLOW FILTRATION COMBUSTION REACTOR

Yu. M. Dmitrenko and R. A. Klyovan[∗]

The non-catalytic process of the synthesis gas (syngas) production via the partial air oxidation of methane in a reversible flow filtration combustion reactor has been investigated experimentally. The effect of the equivalence ratio and specific mass flow rate of the fuel mixture on the conversion products composition and maximum temperature within the reaction zone have been studied. The optimal conditions for the process, which provide the most effective conversion of methane to syngas, have been determined.The maximum hydrogen concentration in syngas has been observed for an equivalence ratio γ = 2.8 and specific mass flow rate g = 1.8 kg/(m²·s).

Introduction. Methane-to-hydrogen conversion is the most extensively used technique to produce hydrogen for chemical industry and hydrogen economy applications. The basic conversion methods are steam reforming (1), partial oxidation (2) and a combination thereof generally referred to as autothermal reforming.

$$CH_4 + H_2O \rightarrow CO + 3H_2 , \tag{1}$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 . \tag{2}$$

The said processes provide a reasonable conversion efficiency but only in the presence of a catalyst. This results in a high capital and production cost which in turn affects the end product value. Therefore, catalytic methods of methane-to-hydrogen conversion are economically sound only in a large scale environment. Thus, for the projected utilization of hydrogen more simple and effective processes have to be found.

One of the most promising non-catalytic techniques is the partial oxidation of methane within a filtration combustion wave propagating downstream in an inert porous medium. Though the reaction of methane partial oxidation per se is an exothermic one, its thermal effect is insufficient for a self-sustained non-catalytic process under adiabatic conditions and so an external heat supply to the reac-

[∗] A. V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; rklyovan@itmo.by

tion zone is needed. On the other hand, an internally-organized heat recuperation between the incoming fuel gas and solid porous medium, which features filtration combustion, results in that the combustion temperature can be much in excess of the adiabatic one. This phenomenon, called "superadiabatic effect" of filtration combustion, is due to the highly developed inner surface of a porous medium, resulting in efficient heat transfer between gas and solid, and dispersion reactants and products in a porous medium, increasing effective diffusion and heat transfer in the gas phase [1]. As a result, no catalyst or external heat supply is needed which makes the process simple and efficient.

The previous studies of the superadiabatic filtration combustion [2-7] have demonstrated the reasonably high efficiency of methane-to-hydrogen conversion (up to 63%) under certain conditions. The main factor governing the process is the combustion temperature which is a function of the equivalence ratio γ and specific mass flow rate g of the incoming fuel mixture.

To put the superadiabatic combustion for hydrocarbons conversion into practice, it is necessary for the filtration process to be made temporally continuous. That can be achieved by the periodic reversal of the gas flow direction through a porous medium.The first application of a reversible flow filtration combustion reactor has related to the development of a burner for extra lean fuel mixtures [8]. A reversible flow system can also be used as a non-catalytic reformer for methane-to-hydrogen conversion [9, 10].

The paper contains the principal results of the detailed experimental investigation of the effect of the fuel mixture composition (γ) and specific mass flow rate (g) on the main conversion parameters.

Experimental setup. The experimental apparatus consists of a reversible flow porous media combustion reactor, reactor preheat unit, gas flow rate control system, gas chromatograph and data acquisition components (fig. 1). The reactor case was made up of a flanged stainless steel tube with an outer diameter of 140 mm and wall thickness of 6 mm. The reaction zone was filled with a randomly packed bed of alumina spheres 5-6 mm in diameter. The packed bed was enclosed by the pressed Kaowool insulation. The gas filtration through the insulation layer is negligible due to its extremely low permeability.

The preheat unit was used to preheat the porous medium for initiation of filtration combustion in the reactor. It's a small porous media burner fueled with methane-air mixture and ignited by a spark plug.

The air and methane for the combustion were taken from a high-pressure line and standard 50-liter high-pressure cylinder, respectively. The flow rates of the components were measured and controlled with «Omega» mass flow controllers. The premixed gas reactants from the mixing chamber were introduced into the reactor at the alternate ends through the periodic switching of the gas flow direction. For that purpose two pairs of «Omega» SV-351 solenoid valves were used. The reaction products were cooled to the room temperature by the water coolers. The laboratory ventilation system was used to remove the exhaust gas out of the room.
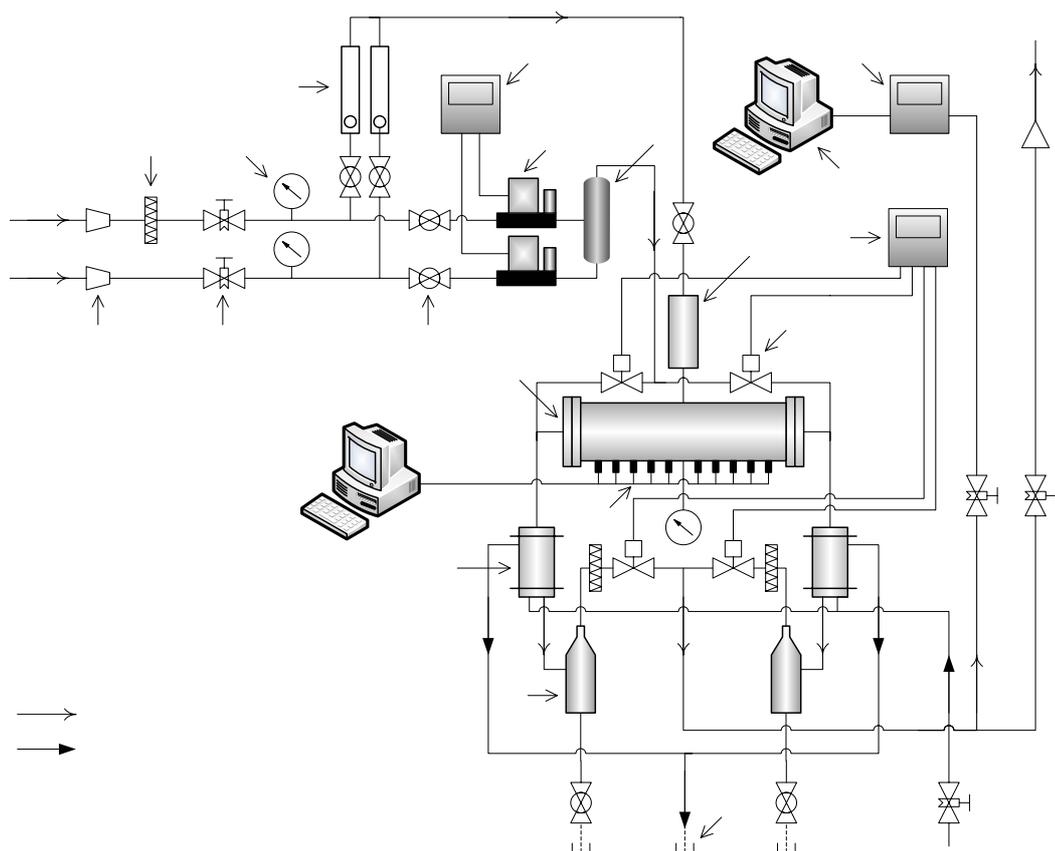

Fig. 1. Schematic of the experimental set up.
    1 – reversible flow filtration combustion reactor, 2 – preheat unit, 3 – thermocouples, 4 – gas reducer, 5 – gas filter, 6 – regulating valve, 7 – manometer, 8 – rotameter, 9 – ball valve, 10 – mass flow controllers control unit, 11 – mass flow controller, 12 – mixing chamber, 13 – solenoid valve, 14 – data acquisition system, 15 – solenoid valves control unit, 16 – gas chromatograph, 17 – water cooler, 18 – condensate tank, 19 – water outlet.

The axial temperature distribution in the porous media reactor was measured with an array of ten S-type thermocouples (Pt/Pt-10%Rh) in a ceramic shell with an exposed junction. A PC based data acquisition system was employed to process the thermocouples readings.

The chemical composition of the output gas was measured with the modified Chrom-4 gas chromatograph. The digital signal processing was performed with an A/D converter based on Analog Devices AD7289 chip. The component separation was achieved with a 3 m long and 3 mm in diameter column filled with molecular sieve CaA. Argon was used as a carrier gas. The output signal from the chromatograph was converted to the digital code and processed by a PC. The calibration of the chromatograph was performed by the reference gas mixtures. After the water vapour removal the concentrations of H_2, O_2, N_2, CH_4 and CO in the output gas were measured.

Results. All the experiments were performed at the minimum operating pressure $P = 2.05$ bar. The lower pressure limit is determined by the total hydraulic loss in the valves, pipelines and reactor porous medium. The half-cycle duration $\tau = 120$ s was held constant for all the flow rates investigated. The time chosen is sufficient for the full development of the reaction zone after the flow direction reversal. For each operating mode, specified by the specific mass flow rate g and equivalence ratio γ, the axial temperature distribution in the reactor and composition of gaseous conversion products were investigated. The experiments have been carried out for four values of γ (2.4, 2.6, 2.8, 3.0) and seven values of g (0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2 kg/(m^2·s)).

At every moment the temperature distribution along the reactor has two maxima. One of them corresponds to the current location of the reaction zone and the other – to the one at the previous reversal cycle of the gas flow. In fig. 2 the temperature profiles in the reactor for one of the modes investigated ($\gamma = 3.0$, $g = 0.6$ kg/(m^2·s)) are given as an example. The profiles correspond to the moments when the combustion front is in the extreme positions within the packed bed, that is, when the gas flow through the reactor is reversed. For the extreme positions of the combustion front its propagation velocity and the maximum temperature of the porous carcass approach their steady-state values. In addition to the temperature profiles corresponding to the extreme positions of the combustion front the averaged profile, which is the simple average thereof, is also given in fig. 2. The maximal oscilla-

tion amplitude of the porous bed temperature was observed at the edges while the minimal one – near the centre.
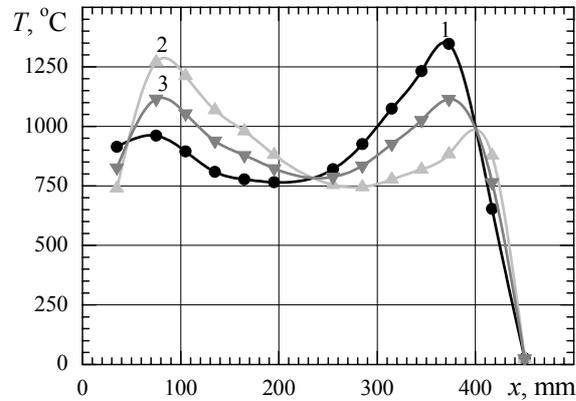

Fig. 2. Axial temperature distributions in the reversible flow reactor corresponding to the extreme positions of the combustion front at its movement: 1 – from right to left; 2 – from left to right; 3 – the averaged profile. $g = 0.6$ kg/(m^2·s), $\gamma = 3.0$, $\tau = 120$ s

The efficiency of methane-to-hydrogen conversion in a reversible flow superadiabatic combustion system directly relates to the maximum reactor temperature T_{max}. There can be distinguished three regions in a wave of filtration combustion of a rich fuel mixture [9]. In the first one, called preheating region, a fresh fuel mixture is heated by the porous carcass. Then at a certain temperature the methane decomposition resulting in the formation of radicals occurs. At the end of the preheating zone, where the gas mixture and packed bed are of approximately equal temperature, a mechanism of an avalanche-like increase of radicals is turned on and the exothermic region follows. In this one relatively fast chemical reactions prevail to result in the dramatic temperature growth and virtually complete consumption of oxygen. According to [9] the characteristic residence time in the exothermic region is about 20 ms, 60% of the total amount of hydrogen being generated there. In the third region, called endothermic one, there prevail endothermic and relatively slow reactions of water and carbon dioxide with residual methane (3, 4):

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO, \tag{3}$$

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO. \tag{4}$$

The gas mixture temperature at the second stage of the process decreases both owing to the heat absorption in the reactions (3, 4) and because of intensive heat removal to the porous carcass. As a result of the endothermic region existence the composition of the conversion products is nonequilibrium.

The effect of the specific mass flow rate g and equivalence ratio γ of the fuel mixture on the maximum temperature T_{max} in the reaction zone is given in fig. 3. The tendency of T_{max} growth with increasing g for all the values of γ is in complete agreement with experimental and numerical simulation results for a single wave of filtration combustion of rich methane-air mixtures [1, 2-4, 10] as well as for combustion of ultra-lean fuel mixtures in a superadiabatic reversible flow reactor [11, 12]. As
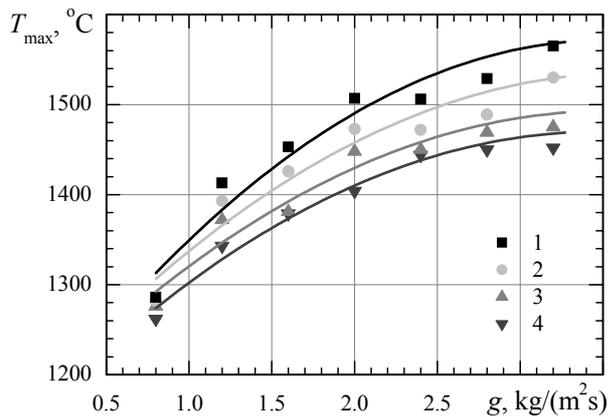

Fig. 3. Dependence of the maximum combustion temperature T_{max} on the fuel mixture specific mass flow rate g for various equivalence ratios γ: 1– 2.4, 2 – 2.6, 3 – 2.8, 4 – 3.0
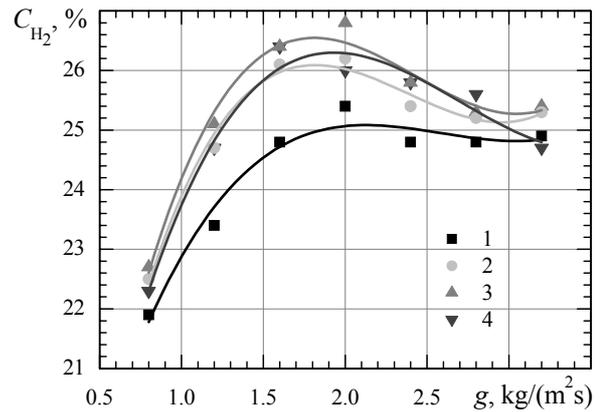
Fig. 4. Dependence of the output hydrogen concentration C_{H2} on the fuel mixture specific mass flow rate g for various equivalence ratios γ

the specific mass flow rate increases the filtration velocity increases; therefore, the superadiabatic effect of filtration combustion intensifies. In addition, the total heat release power also increases; hence, a relative fraction of heat loss from the reactor in the general heat balance decreases. Thus, the maximum temperature increases as the specific mass flow rate increases.

The chromatographic analysis of the gaseous conversion products composition enabled to estimate the efficiency of the process under consideration in terms of such key parameters as the output hydrogen and residual methane concentrations as well as methane-to-hydrogen conversion level. The output hydrogen concentration data are shown in fig. 4. The growth of the hydrogen yield with increasing specific mass flow rate can be accounted for that the chemical reaction kinetics improves as the combustion temperature increases. The hydrogen concentration reaches its maximum at $g \approx 1.8$ kg/(m^2·s). The existence of the maxima in the dependence of the hydrogen concentration on the specific mass flow rate can be ascribed to the opposite effect of two factors. On the one hand, the hydrogen yield in the exothermic region of a filtration combustion wave (fig. 4) increases with the maximum temperature in the reaction zone (fig. 3) which in turn increases as the specific mass flow rate

increases. On the other hand, the residence time of the gas mixture in the endothermic region is inversely proportional to the filtration velocity, i.e., specific mass flow rate. Therefore, an amount of hydrogen generated in the relatively slow endothermic reactions decreases as the specific mass flow rate increases.

The residual methane concentration in the product gas and methane-to-hydrogen conversion level η are the most sensitive parameters of the conversion efficiency. The former (fig. 5) decreases as the specific mass flow rate increases and equivalence ratio decreases. The minimum methane concentration was observed for $\gamma = 2.4$ and $g \approx 1.8$ kg/(m²·s). The residual methane concentration rise at $g > 1.8$ kg/(m²·s) seems to be accounted for the same reason as the hydrogen concentration decrease, that
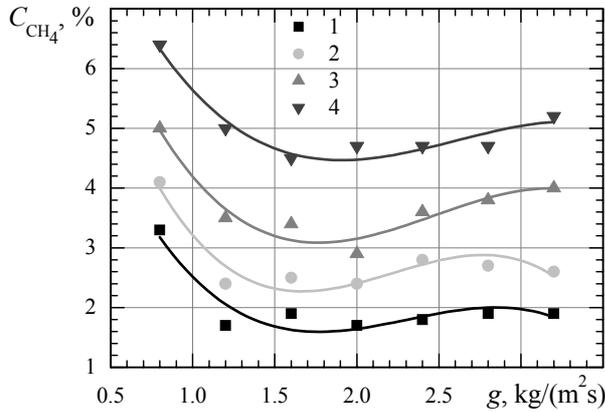

Fig. 5. Dependence of the residual methane concentration C_{CH4} on the fuel mixture specific mass flow rate g for various equivalence ratios γ
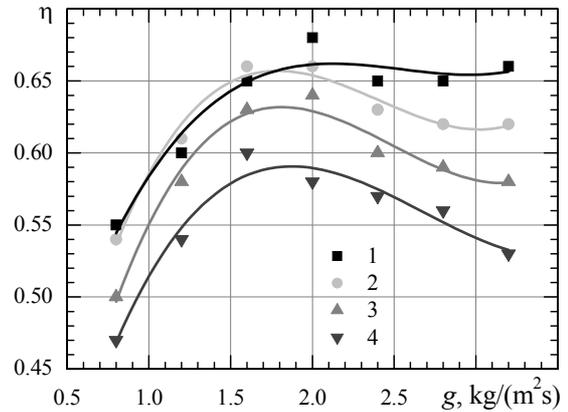
Fig. 6. Dependence of the methane-to-hydrogen conversion level η on the fuel mixture specific mass flow rate g for various equivalence ratios γ

is, for the residence time decrease in the endothermic region to a level at which the methane consumption rate in the reactions (3, 4) decreases.

The methane-to-hydrogen conversion level, which defines a hydrogen fraction in methane to be converted into free hydrogen, can be estimated in terms of the input and output concentrations of N_2, H_2 and CH_4 as follows:

$$\eta = \frac{C_{H_2} C_{N_2}^{in}}{2 C_{CH_4} C_{N_2}^{out}},$$
(5)

where $C_{N_2}^{in}$, C_{CH_4} – the volume concentrations of nitrogen and methane in the incoming gas mixture;

C_{H_2}, $C_{N_2}^{out}$ – the output volume concentrations of hydrogen and nitrogen, respectively. Fig. 6 depicts

the methane-to-hydrogen conversion level η depending on g and γ. A behavior of η depending on g is the same as of the hydrogen concentration – the optimal value of g is in the range of $1.8 \div 2.0$ kg/(m^2·s) for all the values of γ. The conversion level increase with the decrease of the equivalence ratio was also observed.

Conclusion. The experimental investigation of the non-catalytic partial oxidation of methane to hydrogen in the reversible flow filtration combustion reactor has been performed. The results obtained enabled to estimate the effect of the composition and specific mass flow rate of the fuel mixture on the conversion process efficiency. The maximum output concentration of hydrogen amounted to 26.8 % at $g = 1.8 - 2.0$ kg/(m^2·s) and $\gamma = 2.8$. Up to 68 % of methane was converted to hydrogen at $g = 1.8 - 2.0$ kg/(m^2·s) and $\gamma = 2.4$. At the lowest operating reactor pressure $P = 2.05$ bar no evidence of soot formation was observed which is the certain advantage of the process. Further investigations are to be carried out to find out the effect of reactor geometry and porous media characteristics on the conversion efficiency.

Nomenclature

C – volume concentration; g – specific mass flow rate, kg/(m^2·s); T –temperature, $^{\mathrm{o}}$C; γ – equivalence ratio; η – conversion level, τ – flow reversal period, s.

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