Introduction

Gas conversion in superadiabatic regime of filtration combustion is a promising means to improve an efficiency of energy saving. In that link, full model consideration of conversion of methane-oxygen-steam mixtures to syngas performed in those conditions became very actual problem. Really, If realized such regime allows one to combine high combustion temperature (hence high yield of hydrogen and carbon monoxide) with low temperature of the gaseous products (i.e. low energy cost of the process). Preliminary assessment of the process was performed under the following assumptions: (1) the reaction zone comprises a stationary wave traveling through the porous medium in the direction of gas flow; (2) gas reactions proceed within a narrow reaction zone; (3) equilibrium composition of reaction products is attained; (4) heat and mass transfer are controlled by gas flow and gas-solid heat exchange; pressure drop on the reactor is negligible [1-2]. The model showed that superadiabatic heating of the gas can be achieved, the combustion temperature depending on both net adiabatic heat effect and apparent ignition temperature, the latter being controlled by the detailed kinetics of gas reactions. The higher is apparent activation energy for gas ignition, the higher superadiabatic heating can be attained, so the high combustion temperature is attainable with lower heat effect. The parametric domain for the gas compositions (oxygen/steam/methane ratios) that provide desirable low net heat effect and favorable equilibrium composition of syngas has been estimated. The favorable compositions are close to oxygen/methane molar ratio 0.6 and water/methane ratio 0.5.

Computational Model Development

Set of Equations

To provide a detailed description for the process, a non-stationary computational model has been developed. The model is based on the following assumptions. The flow of the reaction mixture is considered as one-dimensional (no distribution of temperature or concentrations in the direction lateral to the reactor axis). Pressure drop on the reactor is negligible. The solid porous medium and gas flow are considered as interpenetrating continua, each characterized by its local temperature and the rate of interphase heat exchange. The reactor is supposed to be perfectly heat-insulated.

The equations set includes energy conservation equations for both solid and gas with interphase heat exchange and heat release rate of chemical reactions; for each gas species a balance equation is written with convection and diffusion flows and kinetic source terms. The equations set is closed with the equation of state for ideal gas, boundary conditions at the reactor ends, and proper initial concentration and temperature distributions related to ignition conditions. The detailed kinetic scheme of the process comprises now 30 species and 121 elementary reactions (without gas-phase formation of soot and its follow heterogeneous transformations). It is quite similar to the well-known GRI-Mech-3 kinetic scheme [3]. Besides, the rate constants for the reactions are those published in popular NIST database [4] and other ones.
**Detailed Kinetic Scheme**

The kinetic scheme accounts for the formation of formaldehyde and active oxygen-methyl radicals, the reactions of direct oxidation of methyl radicals, and the reactions of direct oxidation for oneself those intermediates too. Additionally to that, the scheme considers the peroxide cycle. The peroxide radicals are formed via oxygen addition to methyl radicals and further react to form the branching methyl-hydro-peroxide. Major active intermediates of initial stage, methanol and formaldehyde, are formed in both cycles. There namely is a basic difference our scheme from Gri-Mech3 data base. The peroxide cycle plays important role on the initial low-temperature stage of the partial methane oxidation. For higher temperature, the main initial mechanism of partial oxidation goes via competing formaldehyde cycle, which included transformations of formaldehyde and others intermediates as the sources of hydrogen. The direct oxidation of formaldehyde (branching) and two reactions of linear decomposition, to H and HCO radicals (branching) and H₂ and CO molecules (decay) proceed only at high temperature. At the consideration of filtration combustion wave propagation ones have been account the soot formation in the gas phase and also a sedimentation of one on a solid surface with follow heterogeneous transformation with methane and water participating.

\[ \text{Figure 1. Concentration of species (mol/cc) vs. time. Initial mixture } \]
\[ \text{O}_2/\text{H}_2\text{O}/\text{CH}_4=0.25/0.83/1; \text{ T}_g=1600 \text{ K; C}_z, \text{ is the volume average concentration of carbon on the porous inert; solid lines, show concentrations calculated disregarding heterogeneous reactions, dotted, with the account thereof.} \]

**Kinetics Calculations disregarding Spatial Distribution of the System Parameters**

For various gas compositions and varied initial temperature preliminary calculations were performed using complete kinetic scheme disregarding spatial distribution. The calculations showed the time evolution of concentrations of products and intermediates and temperature. For initial temperature of 1000 K the reaction time (typical time for reaching maximum temperature) is on the order of 1 s. For mixtures richer in
methane, the reaction time is longer and the maximum temperature is lower. The composition of products at maximum temperature is far from established one, the concentration of intermediates remains high. The typical reaction time for water conversion, however, is order of magnitude longer than the reaction time for oxidation.

Also important are the reactions involving carbon that is deposited on the surface of inert porous solid. Figure 1 shows the calculated concentrations of species vs. time for a model ultra-rich mixture of $O_2/H_2O/CH_4=0.25/0.83/1$ with the kinetic schemes regarding and disregarding contribution of heterophase reactions, including interaction between water and carbon.

Figure 2 shows the calculated concentrations of species vs. time for a model ultra-rich mixture of $O_2/H_2O/CH_4=0.25/0.83/1$ with the kinetic schemes regarding and disregarding contribution of heterophase reactions, including interaction between water and carbon.

In both cases, oxygen is consumed fast. Further relatively slow conversion of water to hydrogen proceeds via heterogeneous reactions. Note (Fig.2) that for the wide variation of initial mixture composition, the consumption of oxygen proceeds much faster than the reactions involving water.

**Numerical Simulation of Down-Flow Traveling Wave of Filtration Combustion**

The modeling of gas mixture conversion in the regime of filtration combustion proved that the traveling wave regimes with superadiabatic heating for conversion of ultra-rich mixtures are attainable. Figure 3 presents spatial distribution of the gas temperature at successive times for different initial heat pulses.

One can see that the traveling wave is formed once the initial heat pulse is sufficiently strong to ignite this ultra rich mixture. Note also that it is primarily overall heat of the pulse and not the maximum temperature that predetermines whether the wave will form or the reaction will fade away.

Figures 4-6 show the effect of gas supply rate on the waves of filtration combustion for a rich methane/oxygen/steam mixture. The velocity of the traveling combustion wave is almost proportional to the gas supply flow rate. Note that the maximum temperature of combustion remains virtually insensitive to the flow rate. Both of these facts are in accord with the predictions of [1] given for a single exothermal reaction.
Note also that in effect, the reaction, for all its complex radical-chain mechanism, is apparently simple one. Indeed, conversion of water in endothermic reactions is negligible. Figure 5 shows that water flow increases in the reaction front due to methane oxidation. Further consumption of water in the reducing atmosphere of products rich combustion is barely discernible due to much slower reaction rate.

Figure 3. Evolution of temperature distribution (ignition of traveling wave). Initial mixture \( \text{O}_2/\text{H}_2\text{O}/\text{CH}_4 = 0.25/0.83/1 \); gas supply rate \( v_g = 30 \text{ cm/s} \); heat exchange coeff. \( \alpha = 2.6E-2 \)

A (squares): Initial heat pulse \( L = 7, T_s = 2000 \text{ K} \); \( t = 1) 305 2) 640 3) 1000 \text{ s} \);
B (solid line): \( L = 10, T_s = 1800 \text{ K} \); \( t = 1) 320 2) 665 3) 1025 \text{ s} \);
C (crosses): \( L = 5, T_s = 2000 \text{ K} \); \( t = 1) 335 2) 651 3) 967 \text{ s} \).

Figure 6 shows that carbon is accumulated continuously in the reducing zone of the combustion wave. The carbon sediment on the solid inert is subsequently consumed by incoming oxygen, when combustion wave reaches a particular location.

**Concluding Remarks**

The above consideration shows that prompt implementation of filtration combustion scheme for conversion of oxygen/ water/ methane mixture to syngas does not meet all the desired goals. The traveling wave with superadiabatic heating is formed indeed. Another favorable feature is that the coking of the porous solid in the combustion wave is but temporary. However, due to the slow reaction rate, the desired steam conversion, which might be anticipated from the thermodynamic calculations, can not be attained in practical time. Steam reforming even does not compensate water formed in methane oxidation. Further efforts are necessary to either develop a catalytic system, which will dramatically accelerate water conversion or increase the combustion temperature in the traveling wave. The superadiabatic heating in the traveling combustion wave provides way to increase the temperature without extra energy expenditure.
Figure 4. Evolution of temperature distribution in the traveling wave. Initial mixture $\text{O}_2/\text{H}_2/\text{CH}_4 = 0.5/1/1$; heat exchange coefficient $\alpha = 2.6 \times 10^{-2}$; A (squares): gas supply rate $v_g = 30 \text{ cm/s}$, $t = 1) 174 2) 393$; B (solid line): $v_g = 60 \text{ cm/s}$, $t = 1) 167 2) 416$; C (crosses): $v_g = 90 \text{ cm/s}$, $t = 1) 181 2) 373$.

Figure 5. Water flow rate (mol/cm$^2$/s) in the traveling wave. The key is the same as Fig. 4.
Figure 6. Concentration of carbon (mol/cc) on the solid inert in the traveling wave. Key is the same as Fig. 4.

Acknowledgments

This work is performed under financial support from Presidium of the Russian Academy of Sciences within frame of the program "Novel approaches to chemistry of fuels and chemical power generation" N 8-024

References


