Simulation of partial oxidation of natural gas in a resource-saving reactor mixer

V Yu Bazhin*, V E Trushnikov and A P Suslov
Saint Petersburg Mining University, Saint Petersburg, Russia

*E-mail: bazhin-alfoil@mail.ru

Abstract. Modern industrial methods of producing hydrogen almost exclusively use fossil fuels, like natural gas, crude oil or coal, as raw materials. Methods such as steam reforming or partial steam oxidation to produce hydrogen from fossil hydrocarbons. This process chemically separates the carbon which is then converted to carbon monoxide (CO). These methods of hydrogen extraction are not ideal to actively protect the climate. There is currently a certain shortage of hydrogen in any refinery, so an additional source of hydrogen needed to stabilize the process. The work presents the results of simulating the processes in the homogeneous zone of the mixer and simulating the process of converting methane in the catalyst bed of the mine reactor using natural gas to produce hydrogen.

The need for hydrogen was increasing year after year due to the constant deepening of oil refining processes, the increasing quality requirements of the fuels and lubricants produced, and the need to desulphurization energy fuels. The raw material base for hydrogen production has changed greatly over the past 25 years. Solid fuel gave way to natural gas, associated oil production gases, oil refining gases and liquid hydrocarbons, for example, light oil distillates, condensates from gas-condensate deposits. The raw material for producing hydrogen by steam catalytic conversion of light hydrocarbons can be natural and factory (dry and fatty) gases, as well as straight run gasoline. Modern hydrogen production plants have a capacity of 300 thousand m$^3$ to 3 million m$^3$ of hydrogen per day; They are characterized by operating pressures in the range of 2-3 MPa. Hydrogen purity in modern plants reaches -99.9995% [1].

The most efficient method of producing hydrogen is the technology of producing hydrogen by catalytic steam reforming of light hydrocarbons in combination with a highly efficient short-cycle process.

Typically steam reformer steam and natural gas are subjected to catalytic cracking at temperatures of about 850-880 °C [2]. The result is a synthetic gas - a mixture of hydrogen, carbon monoxide (CO) and carbon dioxide (CO$_2$). Carbon monoxide is converted to steam CO$_2$ in a subsequent CO reforming reaction step in which more hydrogen is produced. Gas with high H$_2$ content in the final steam state at the stage of subsequent CO reforming reaction, at which more hydrogen is generated. Steam two-stage methane conversion is the most common way to produce hydrogen.
In our case, the results of simulating processes in the homogeneous zone of the mixer and simulating the conversion process in the catalyst bed of the mine reactor are presented with the use of the natural gas that has been purified, which allow and develop a method and device for obtaining thermal energy, which is produced by burning this natural gas in the upper zone of the mine reactor in a special mixer [1]. This in turn increases the amount of converted hydrogen-containing gas, which is no longer used as a heat energy source or an additional source in the refinery as a reactant.

Secondary conversion shaft reactor is designed to carry out practically complete conversion of methane remaining in the converted reactor after the tubular reactor [1]. The reactor in addition to producing the nitrogen-hydrogen mixture can also be used for other processes, including for producing hydrogen and methanol [2].

Methane conversion is also carried out by partial oxidation in main reaction (1).

$$\text{CH}_4 + 0.5\text{O}_2 = 2\text{H}_2 + \text{CO} + 36 \text{kJ/mol}, \quad (1)$$

In carrying out the process of this reaction, hydrogen yield is significantly increased, as a result of the studies carried out, the design of the mixer has been developed, the schematic diagram of which is shown in paper [3]. The reactor mixer consists of an oxygen axial inlet channel supplied with a temperature of 453 K. In its upper part there is a natural gas supply channel supplied with a temperature of 623 K, with flow swirlers in the lower part of the channel. Lower part of mixer has expansion, in volume of which reaction of partial oxidation of methane takes place. Outside this chamber flows the flow of steam-gas mixture, with temperature 773 K, coming from the line of steam-gas mixture supply to the tubular reactor of primary methane conversion. The converted gas from the primary conversion tube reactor at 1063 K is fed to the top of the reactor, flows around the mixer and enters the catalyst bed. The surface separating the partial conversion reaction zone is not only cooled by the vapor-gas mixture stream.

The reaction of double steam conversion of methane (2) takes place when thermal energy is supplied.

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO} – 206 \text{kJ/mol}, \quad (2)$$

This surface can be seen as a partition on which exo- and endothermic reactions simultaneously occur. When modeling the process, it is necessary to know the nature of the flow and the boundaries of the thermodynamic modes of the process, the physical and chemical mechanism of which is based on the transfer of mass, the amount of movement (impulse) and energy (figure 1).

**Figure 1.** Schematic diagram of operation of special methane partial oxidation mixer.
It is necessary to know that modeling the process the nature of the flow and the zones of the thermodynamic modes of the process and the physical and chemical mechanism of which is based on mass transfer, quantity of movement (impulse) and energy (figure 2) [2].

Mathematical modeling ultimately allows to quantify optimal parameters of processes and devices and to determine ways and methods of improvement of production hydrogen technology. One of the directions in modeling is the unification of mathematical models in which the modeling process itself is greatly facilitated by the accumulation of such models and their identification and using.

In the papers [3, 4], considering that processes of heat transfer through the reactor partition with simultaneous implementation of exo- and endothermic processes for mathematical modeling of the process of CH₃OH synthesis was carried out to obtain a hydrogen mixture.

Figure 2. Diagram of the process of simultaneous exo- and endothermic reactions.

Since the theory allows to describe such processes using mathematical modeling methods, the processes taking place in the lower expanding part of the methane and oxygen mixer have been considered [5].

The equations of material and thermal balance are generally (3,4):

\[
- \frac{\partial X_i}{\partial Z} + \frac{D_i}{u_i} \cdot \frac{\partial^2 X_i}{\partial L^2} + \frac{\rho_i M_i}{G_i y_i} (-r_i) = 0 ,
\]

\[
- \frac{\partial T_i}{\partial Z} + \frac{k_{ei}}{G_i C_{Pi}} \cdot \frac{\partial^2 T_i}{\partial L^2} + \frac{\rho_i(-\Delta H_i^0)}{G_i C_{Pi}} (-r_i) = 0 .
\]

For the channel for supply of the mixture of water vapor and methane in the ratio of 3.6:1, respectively, in which the endothermic reaction takes place, the surface of the mixer is cooled, the equations of material and thermal balances have the form (5, 6):

\[
\frac{\partial X_1}{\partial L} = - \frac{1}{D_1 \cdot C_1} \cdot (-r_1) ,
\]

\[
-k_{ei} \frac{\partial T_1}{\partial L} = \frac{(T_w - T_1)}{1 + \frac{d_{II}}{h_{W1} \cdot \lambda_{II}}} + \frac{(-\Delta H_1^0)}{1 + \frac{1}{h_{W1} \cdot \lambda_{II}}} \cdot (-r_1) .
\]
For the channel in which the exothermic partial oxidation reaction of methane is carried out, the material and thermal balance equations (7, 8):

\[
\frac{\partial X_2}{\partial L} = \frac{1}{D_2 \cdot C_2} \cdot (-r_2),
\]

(7)

\[
-k_{e2} \frac{\partial T_2}{\partial L} = \left( \frac{T_2 - T_{\omega}}{1 + \frac{d_{II}}{\lambda_{II}}} \right) + \frac{(-\Delta H_2^0)}{1 + \frac{d_{II}}{\lambda_{II}}} \cdot (-r_2).
\]

(8)

At the center of the mixer, the process conditions correspond to the following characteristics (9):

\[
\frac{\partial X_u}{\partial L} = 0, \quad \frac{\partial T_u}{\partial L} = 0.
\]

(9)

Conditions of parameters on mixer partition (interface) on the side of endothermic and exothermic reactions are equal to (10,11) under assumed assumptions:

\[
\frac{\partial X_1}{\partial L} = 0, \quad -k_{e1} \frac{\partial T_1}{\partial L} = \left( \frac{T_{\omega} - T_1}{1 + \frac{d_{II}}{\lambda_{II}}} \right),
\]

(10)

\[
\frac{\partial X_2}{\partial L} = 0, \quad -k_{e2} \frac{\partial T_2}{\partial L} = \left( \frac{T_2 - T_{\omega}}{d_{II} + \frac{1}{\lambda_{II}}} \right).
\]

(11)

where: \( C \) - concentration of reagents, \( \text{mol/m}^3 \); \( Z \) - axial coordinate, \( \text{m} \); \( C_P \) - heat capacity of gas mixture components, \( \text{kJ/kg} \cdot \text{K} \); \( X \) - dimensionless coordinate; \( D \) - effective diffusion coefficient, \( \text{m}^2/\text{h} \); \( u \) - gas velocity, \( \text{m/h} \); \( L \) - partition length, \( \text{m} \); \( \rho \) - partial pressure, \( \text{MPa} \); \( M \) - mass of flow, \( \text{kg} \); \( (-r) \) - reaction rate, \( \text{mol/kg} \cdot \text{h} \); \( T \) - temperature, \( \text{K} \); \( G \) - the mass of the flow passing through the unit surface, \( \text{kg/m}^2 \cdot \text{h} \); \( \gamma \) - a dimensionless molar fraction of the reactive component of the gas; \( k_e \) - specific thermal conductivity, \( \text{Wt/m} \cdot \text{K} \); \( (-\Delta H_i^0) \) - enthalpy of reagents, \( \text{J/mol} \); \( d_{II} \) - partition thickness, \( \text{m} \); \( \lambda_{II} \) - thermal conductivity of the partition, \( \text{Wt/m} \cdot \text{K} \).

The modelling of the steam-oxygen methane conversion process with partial oxidation in a special mixer with technical oxygen containing 95% \( \text{O}_2 \) and 5% \( \text{N}_2 \) (volume) was performed on the assumption that the ratio between \( \text{CO} \) and \( \text{CO}_2 \) in determining the composition of the converted gas obtained in the mixer prior to mixing with the converted gas coming from the primary reforming tube furnace corresponds to the equilibrium of the \( \text{CO} \) reforming reaction with steam.

General ratio gas:steam in the mixer made 1:1.1. The calculation was performed on 1000 \( \text{m}^3 \) \( \text{CH}_4 \). The steam volume was 1100 \( \text{m}^3 \), the oxygen supply by stochiometric was 500 \( \text{m}^3 \). The gas composition
at the mixer outlet at 1273 K is obtained as follows: CO₂ - 290 m³, CO - 635 m³, H₂ - 2180 m³, CH₄ - 47 m³, N₂ - 40 m³.

In the actual process, the catalyst activity is reduced during operation, and in order to provide residual methane at the outlet of the methane conversion reactor, it will be necessary to slightly increase the temperature of the process gas in front of the catalyst bed, which is achieved by adding additional technical oxygen [6,7]. Thermal energy in this case is obtained by the reaction, due to the increase in oxygen content more than stoichiometric (12).

\[ \text{CH}_4 + 2 \text{O}_2 = \text{CO}_2 + 2 \text{H}_2\text{O} + 892 \text{ kJ/mol}, \quad (12) \]

Thus, given that about 400 m³ of natural gas is consumed in the primary steam conversion of methane in the tubular reactor for the conversion of 1000 m³ of methane, the simulation of the process in question shows that the mixer in question will produce about 20-25% of the saving of natural gas for hydrogen production.

Reference
[1] Habibullin R R 1990 *Operation of hydrogen and synthesis gas production plants* (Moscow: Chemistry) p 45-53
[2] Hydrogen 1989 *Properties, acquisition, storage, transportation, application* (Moscow: Chemistry) p 49-60
[3] Trushnikov V E and Arzhanyh A M 2009 Modeling of heat exchange process Through the partition in exo- and endothermic reactions to Resource saving in methane *The 8th Between - Of the National Scientific Conference "Resource-reproducing, Low-waste and environmental technologies for subsoil development* p 178-81
[4] Fukuhara C and Igarashi A 2005 Performance simulation of a wall- type reactor in which exothermic and endothermic reactions proceed simultaneously, comparing with that of a fixed- bed reactor *Chem. Eng. Sci.* 2005 60(24) 6824-34
[5] Kolios G, Frauhammer J and Eigenberger G 2002 Efficient reactor concepts for coupling of endothermic and exothermic reactions *Chem. Eng. Sci.* 57(9) 1505-10
[6] Linde A G 2014 *Gasification technology* (Munich)
[7] Jones W P and Mc Quirk J 1980 Computation with Mathematical Modelling of Gas Turbine Combustion Chambers *AGARD Conf. Proc* 275 12-23
[8] Spalding D B 1972 A Two- Equation Model of Turbulence *VDI- Forsch. Heft-549* pp 5-16