

THERMODYNAMIC ANALYSIS OF CARBON FORMATION CONDITIONS IN A STEAM METHANE REFORMING PROCESS

by

Dmitry PASHCHENKO* and Maria GNUTIKOVA

Samara State Technical University, Samara, Russia

Original scientific paper

<https://doi.org/10.2298/TSCI190404136P>

Thermodynamic equilibrium analysis of the steam methane reforming process to synthesis gas was studied. For this purpose, the system of chemical reactions for carbon production and consumption as well as other side reaction in the steam methane reforming process were analysed. The material balance and the equations of law mass action were obtained for various chemical reactions. The system of those equations were solved by dichotomy method. The investigation was performed for a wide range of operational conditions such as a temperature, pressure, and inlet steam-to-methane ratio. The results obtained, with the help of developed algorithms, were compared with the results obtained via different commercial and open-source programs. All results are in excellent agreement. The operational conditions for the probable formation of carbon were determined. It was established that for the temperature range above 1100 K the probability of carbon formation is absent for steam-to-methane ratio above units. The presented algorithm of thermodynamic analysis gives an appearance of the dependence of the product composition and the amount of required heat from operating conditions such as the temperature, pressure and steam-to-methane ratio.

Key words: *methane, steam methane reforming, hydrogen, heat balance, thermodynamic analysis, thermodynamic analysis*

Introduction

Steam methane reforming is one of the vital methods for production of hydrogen, CO, or synthesis gas from natural gas that mainly consists of CH₄ [1-7]. This is achieved in the processing set-ups which reacts steam with CH₄ at high temperature with CH₄. This set-up is known as the steam methane reformer. The steam methane reformer is also widely used in fuel cells for hydrogen production [8-10]. There is also interest in using the steam CH₄ reforming reaction for thermochemical recuperation of waste flue gases heat [11-16].

It is generally known that the efficiency of the steam methane reforming process significantly depends on operational parameters such as temperature, pressure, and composition of the inlet reaction mixture [17-19]. In addition, the composition of reformed products (reformate) in real reformers also depends on the type of catalyst, the mass of catalyst, and the form and method of filling the reaction space [20-26]. However, it is known that modern high performance catalysts aid in retrieving the composition of reformed products at the outlet, which is close to the equilibrium [27, 28]. Therefore, researchers and engineers pay significant attention the determination of equilibrium compositions (maximally achievable concentrations) of reformed products as a function of operating parameters such as temperature, pressure, and inlet gas composition.

* Corresponding author, e-mail: pashchenkodmitry@mail.ru

The effects of temperature, pressure, and inlet gas composition on equilibrium reformate compositions can be calculated using thermodynamic analysis. In recent years thermodynamic equilibrium results by using the Gibbs free minimization method for steam methane reforming have been published by different 25 specialists [17, 19, 29, 30]. The wide development of specialized software significantly simplified the implementation of thermodynamic analysis of steam methane reforming. The researcher uses quite literally just a few mouse clicks away in setting operational parameters (temperature, pressure, feed gas composition) and after a few seconds is getting the result. Various commercial and open-source programs are used for modelling and simulating the steam methane reforming process. For example, Aspen HYSYS [18, 19], IVTANTHERMO [31, 32], CHEMCAD [33], Chemkin, ProVision, *etc.*, are all programs that are using different databases and algorithms to calculate the equilibrium gas composition.

In the author's previous work for the thermodynamic analysis of propane reforming the program IVTANTHERMO was used [18, 34]. The main difference of this software is the use of different databases for the process modelling. At the same time, the results obtained with Aspen and IVTANTHERMO for propane reforming are almost identical.

Sun *et al.* [35] presented thermodynamic study of steam methane reforming process via FactSage software. The equilibrium compositions are determined by minimizing the Gibbs free energy for a given set of species without any specification of the possible reactions which might take place in the steam methane reformer. Minimization is accomplished with the use of FactSage software capable of performing analysis of single or multiple-phases of several components in equilibrium.

The works mentioned previously consider the algorithm for calculating the equilibrium composition as a *black box* in which it is difficult to establish the effect of operational parameters on the result of the calculation. In addition, it is difficult for the starting investigators to see the relationship between the calculation results and the initial data. One of the simplest and obvious ways to perform a thermodynamic analysis of CH₄ steam conversion is to conjugate solve the integral material balance equations and the mass action law equations for the steam methane reforming process. The use of this method makes it possible to obtain a visual relationship between the initial data and the calculation results. Moreover, the conjugate solution of the integral material balance equations and the mass action law equations makes it possible to determine the boundary conditions for the carbon formation in the steam reformer.

The main goals of the present work are:

- to develop and describe the algorithm of thermodynamic analysis based on the conjugate solution of the integral material balance equations and the mass action law equations,
- to analyze the chemical reactions in the steam methane reforming system, and
- to calculate and verify the results of thermodynamic analysis.

Chemical mechanism

The flow diagram for substance flows in the steam methane reformer is shown in fig. 1. For analyzing the process, it is further assumed that a mixture of pure CH₄ and pure steam is supplied to the reformer. For more accurate calculations it is necessary to take into account the presence of impurities of hydrocarbons, nitrogen, and other components in the gas-flow.

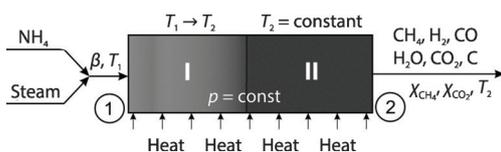


Figure 1. The flow diagram for substance flows in the steam methane reformer

The overall reaction in the steam methane reformer to form H₂, C, CO, CO₂, H₂O and other components may include the equations listed in tab. 1 [20]. In addition, other chemical reactions may occur in the reformer, which are basically a combination of the reactions shown in the tab. 1. However, it is well known that for thermodynamic analysis it is sufficient to consider only elementary reactions presented in tab. 1.

On the basis of the Gibbs free energy minimization technique from several possible reactions, the most probable reaction is reaction with a minimum change of the Gibbs free energy. There are many articles that consider the algorithm for the determination of Gibbs free energy [18, 19]. For a system at chemical equilibrium the Gibbs free energy for each reaction can be determined:

$$\Delta G^\circ = -RT \ln K_{eq(i)} \quad (1)$$

where R is the gas constant, T – the temperature (for analyzed scheme T is equal T₂ according fig. 1), and K_{eq(i)} – the equilibrium constant of i-reaction.

Figure 2 shows the dependence of the Gibbs free energy vs. temperature for reactions presented in tab. 1. As it can be seen from fig. 2, the Gibbs free energy for oxidation reactions (1 and 3 from tab. 1) decreases significantly with increasing temperature. In the temperature range above 900 K, reforming reactions (1 and 3 from tab. 1) are more likely to be thermodynamic than the reactions of CH₄ cracking – 4, and Boudouard reaction – 5. At temperatures above 1000 K, the equilibrium of the reactions (6 and 7 from tab. 1) is shifted toward the formation of gasification products of the carbon.

Table 1. Possible chemical reactions in the reformer [20]

	Reaction	ΔH_{298} [kJmol ⁻¹]
	Methane oxidation	
1	CH ₄ + H ₂ O ⇌ CO + 3H ₂	206.4
2	CO + H ₂ O ⇌ CO ₂ + H ₂	-41.1
3	CH ₄ + CO ₂ ⇌ 2H ₂ + 2CO Carbon formation	247.3
4	CH ₄ ⇌ C + 2H ₂	74.8
5	2CO ⇌ C + CO ₂	-173.3
6	CO + H ₂ ⇌ C + H ₂ O	-90.13
7	CO ₂ + 2H ₂ ⇌ C + 2H ₂ O	-131.3

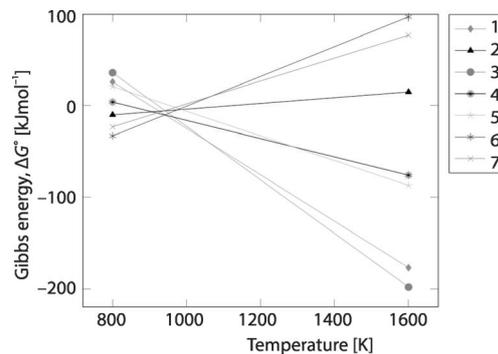


Figure 2. The Gibbs free energy as a function of temperature for reactions in tab. 1

Methodology

The material-balance equation for the chemical-technological system, fig. 1, for the steady-state condition can be transcribed:

$$\sum_{j=1}^l \dot{n}_{i,j} = 0 \quad (2)$$

where $\dot{n}_{i,j}$ [mols⁻¹] is the molar flow rate of i-element through j inlet (or outlet), l – the total number of inlets and outlets. The flows to the reformer is considered as positive, and the flows from the reformer are negative.

For further analysis at the reformer inlet j = 1, at the reformer outlet j = 2. Then the equation of material balance for carbon takes the form:

$$\dot{n}_{CH_4,1} - \dot{n}_{CH_4,2} - \dot{n}_{CO,2} - \dot{n}_{CO_2,2} = 0 \quad (3)$$

The equation of material balance for oxygen:

$$\dot{n}_{\text{H}_2\text{O},1} - \dot{n}_{\text{H}_2\text{O},2} - \dot{n}_{\text{CO}_2} - 2\dot{n}_{\text{CO}_2,2} = 0 \quad (4)$$

The equation of material balance for hydrogen:

$$4\dot{n}_{\text{CH}_4,1} + 2\dot{n}_{\text{H}_2\text{O},1} - 2\dot{n}_{\text{CO}_2} - 2\dot{n}_{\text{CO}_2,2} = 0 \quad (5)$$

The material balance eqs. (3)-(5) allow to minimize the number of parameters describing the resulting change in the composition of the reaction mixture at the reformer outlet. This significantly facilitates the subsequent analysis of the functioning of the system.

The inlet gas mixture composition can be unambiguously determined:

$$\beta = \frac{\dot{n}_{\text{CH}_4,1}}{\dot{n}_{\text{H}_2\text{O},1}} \quad (6)$$

The reformat composition can be determined by two parameters:

$$X_{\text{CH}_4} = \frac{\dot{n}_{\text{CH}_4,1} - \dot{n}_{\text{CH}_4,2}}{\dot{n}_{\text{CH}_4,1}}, \quad X_{\text{CO}_2} = \frac{\dot{n}_{\text{CO}_2,2}}{\dot{n}_{\text{CH}_4,1}} \quad (7)$$

The first parameter is the CH₄ conversion degree. The second is the degree of CH₄ conversion CO₂.

Therefore, the composition of the outlet products can be expressed using parameters β , X_{CH_4} , and X_{CO_2} .

The CH₄:

$$\dot{n}_{\text{CH}_4,2} = \dot{n}_{\text{CH}_4,1} (1 - X_{\text{CH}_4}) \quad (8)$$

Carbon monoxide:

$$\dot{n}_{\text{CO}_2} = \dot{n}_{\text{CH}_4,1} (X_{\text{CH}_4} - X_{\text{CO}_2}) \quad (9)$$

Steam:

$$\dot{n}_{\text{H}_2\text{O},2} = \dot{n}_{\text{CH}_4,1} (\beta - X_{\text{CH}_4} - X_{\text{CO}_2}) \quad (10)$$

Hydrogen:

$$\dot{n}_{\text{H}_2,2} = \dot{n}_{\text{CH}_4,1} (3X_{\text{CH}_4} + X_{\text{CO}_2}) \quad (11)$$

For these equations $X_{\text{CO}_2} < X_{\text{CH}_4} < 1$ and $\beta > (X_{\text{CO}_2} + X_{\text{CH}_4})$.

Assuming that at sufficiently high temperatures maintained during steam methane reforming, the reagents exhibit the properties of ideal gases (in the sense that the chemical potentials of the components are determined by their partial pressures), the equilibrium constant for water-gas shift reaction can be written:

$$K_{\text{eq,wgs}} = \frac{P_{\text{H}_2} \cdot P_{\text{CO}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}} \quad (12)$$

The equilibrium constant, eq. (12), can be expressed by molar fraction of each species:

$$K_{\text{eq,wgs}} = \frac{x_{\text{H}_2} \cdot x_{\text{CO}_2}}{x_{\text{CO}} \cdot x_{\text{H}_2\text{O}}} \quad (13)$$

where $x_i = \frac{\dot{n}_{i,2}}{\sum \dot{n}_{i,2}}$. Moreover, here $\sum \dot{n}_{i,2} = \dot{n}_{\text{CH}_4,1} (1 + 2X_{\text{CH}_4} + \beta)$.

Therefore, from eq. (13), on the basis of eqs. (9)-(11), the following equation can be obtained:

$$\dot{n}_{\text{CH}_4,1}^2 (3X_{\text{CH}_4} + X_{\text{CO}_2}) X_{\text{CH}_4} - K_{\text{eq,wgs}} \dot{n}_{\text{CH}_4,1}^2 (X_{\text{CH}_4} - X_{\text{CO}_2}) (\beta - X_{\text{CH}_4} - X_{\text{CO}_2}) = 0 \quad (14)$$

This equation can be represented as a quadratic equation:

$$aX_{\text{CO}_2}^2 + bX_{\text{CO}_2} + c = 0 \quad (15)$$

where $a = 1 - K_{\text{eq,wgs}}$, $b = 3X_{\text{CH}_4} + K_{\text{eq,wgs}}\beta$, and $c = -K_{\text{eq,wgs}}X_{\text{CH}_4}(\beta - X_{\text{CH}_4})$.

In eq. (15) $b > 0$, and $c < 0$ because $\beta > X_{\text{CH}_4}$. The eq. (15) has two roots:

$$X_{\text{CO}_2} = \frac{-b - \sqrt{b^2 - 4ac}}{2a}, \quad X_{\text{CO}_2} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (16)$$

If $K_{\text{eq,wgs}} > 1$ (at the temperature range below 1090 K), then $a < 0$, and therefore, $(b^2 - 4ac > b)^{1/2}$ and both roots of eq. (15) are positive. However the root with "-" before $(b^2 - 4ac > b)^{1/2}$ does not satisfy condition $X_{\text{CO}_2} < X_{\text{CH}_4}$, due to fact:

$$\frac{-b - \sqrt{b^2 - 4ac}}{2a} > \frac{b}{|a|} > \frac{K_{\text{eq,wgs}}\beta}{K_{\text{eq,wgs}} - 1} > \beta > X_{\text{CH}_4} \quad (17)$$

At high temperatures ($T > 1100$ K) $K_{\text{eq,wgs}} < 1$, therefore, $a > 0$, and the root with "-" before $(b^2 - 4ac > b)^{1/2}$ also does not satisfy, since in this case it is less than zero. Hence it follows that there exists a unique solution of eq. (15) that has a physical meaning:

$$X_{\text{CO}_2} = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \quad (18)$$

The eq. (15) allows us to exclude X_{CO_2} as the independent parameter of the system, associating it with the parameters β , X_{CH_4} and T_2 (by $K_{\text{eq,wgs}}$). According to fig. 1, a constant temperature T_2 is maintained at a sufficiently large area near the reformer outlet. It should be expected that in the reacting mixture an equilibrium composition of all the elements will be taking place. In order to determine the degree of CH_4 conversion it is necessary to solve, with respect to X_{CH_4} , an equation describing the equilibrium with respect to the first reaction (according to tab. 1) (equilibrium in the WGS reaction is already taken into account in eq. (15)):

$$K_{\text{eq,wgs}} = \frac{P_{\text{H}_2}^3 \cdot P_{\text{CO}}}{P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}} = \frac{x_{\text{H}_2}^3 \cdot x_{\text{CO}}}{x_{\text{CH}_4} \cdot x_{\text{H}_2\text{O}}} P^2 \quad (19)$$

where P is the total pressure in the reformer.

The eq. (19) implicitly determines the required dependence X_{CH_4} vs. T_2 . The solution of this equation with respect to X_{CH_4} , in view of its non-linearity and the dependence of the right-hand side on T_2 can be carried out by the different numerical methods. For this thermodynamic analysis, the dichotomy method was used to determine the degree of CH_4 conversion.

Figure 3 shows the equilibrium changes of the degree of CH_4 conversion as a function of temperature when the different inlet gas compositions are introduced into the steam methane reforming reaction system at the various pressure. Steam additions have a noteworthy effect on the degree of CH_4 conversion. The addition of extra steam to the feed stream increased CH_4 conversion considerably; especially at temperatures below 1200 K which is consistent with the works of other authors [19]. They reported that the addition of steam increased CH_4 activity. Above 1200 K, the degree of CH_4 conversion is obtained about maximum value (about 100%). This fact also has a worthy correlation with the articles of other authors [16].

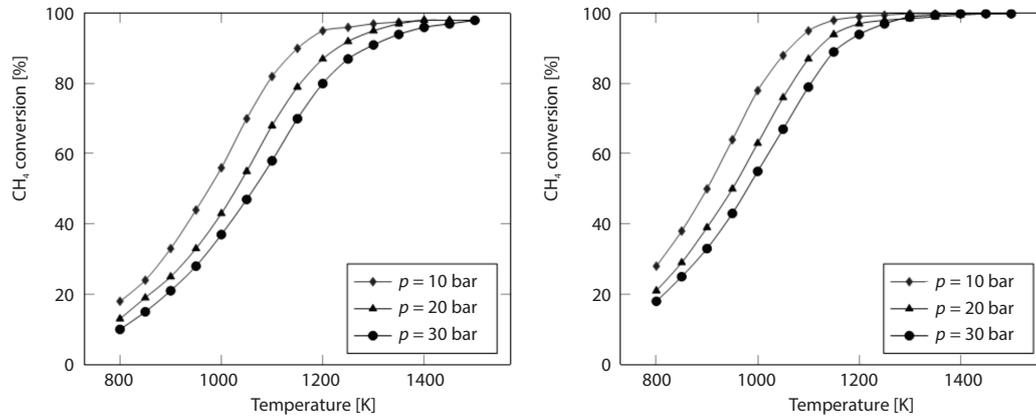


Figure 3. Effect of temperature on the equilibrium degree of CH_4 conversion for the various pressure; (a) $\beta = 2$ and (b) $\beta = 4$

The trends in figure 3 indicates that decreasing pressure shifted steam reforming reaction in the direction of more CH_4 consumption. This is a consequence of the Le-Chatelier's principle. When steam CH_4 reforming system at equilibrium is subjected to change in pressure, then the system readjusts itself to counteract (partially) the effect of the applied change and a new equilibrium is established. In other words, whenever a system in equilibrium is disturbed the system will adjust itself in such a way that the effect of the change will be nullified. This fact can be explained by eq. (19) where right side of the equation is concluding the total pressure in the reformer.

To verify this developed algorithm the results were compared with the results that were obtained via the commercial and open-source softwares: Aspen HYSYS, and IVTAN-THERMO, tab. 2. All results are in excellent agreement with the simulated data obtained via these special programs.

Table 2. The comparison of the reformat composition, % [molmol⁻¹]

Temperature	Pressure	Source	Gas composition [%]				
			H ₂	CO	H ₂ O	CO ₂	CH ₄
1000 K	1 bar	IVTAN	63.01	14.32	16.32	5.23	1.12
		ASPEN	63.40	14.38	16.12	5.08	1.02
		Algorithm	63.42	14.43	16.11	5.12	0.92
1000 K	5 bar	IVTAN	60.66	14.82	17.32	5.55	1.65
		ASPEN	61.60	14.98	17.92	4.08	1.42
		Algorithm	61.44	14.93	17.97	4.18	1.48
1100 K	1 bar	IVTAN	63.88	16.08	16.02	3.93	0.09
		ASPEN	63.65	16.14	16.15	3.98	0.08
		Algorithm	63.76	16.11	16.11	3.94	0.08
1100 K	5 bar	IVTAN	61.28	15.02	17.87	4.24	1.59
		ASPEN	61.57	14.99	17.88	4.11	1.45
		Algorithm	61.45	14.93	17.96	4.18	1.48

With the help of the material balance equations it is possible to determine absolute volume of hydrogen at the reformer outlet. Figure 4 shows that the number of moles of hydrogen increases when temperature and β ratio increasing. It was established that for the high temperature more than three mole of hydrogen can be produced for each mole of CH_4 , while the equilibrium composition for steam methane reforming reaction, reaction – 1 according to tab. 1 gives is only three mol. Other hydrogen is produced by water-gas shift reaction. That is why the water-gas shift reaction must be taken into account for the thermodynamic analysis of the steam methane reforming process.

Figure 5 displays the equilibrium compositions as a function of the temperature and for the $\beta = 2$ and $p = 10$ bar. From this graph it can be seen that the CH_4 conversion, as well as the H_2/CO ratio, increases when increasing the temperature is in the steam methane reformer. As can be seen previously, a simple and intuitive algorithm of thermodynamic analysis makes it possible to determine the equilibrium composition of the steam methane reforming process without the use of commercial software. In addition, the developed algorithm shows the apparent dependence of operational parameters, such as temperature, composition of the initial mixture, and pressure on the equilibrium composition.

There are some hints that significantly simplify thermodynamic analysis in the temperature range above 1200 K (usually steam CH_4 conversion is carried out at temperatures above 1100-1200 K) and in the temperature range below 700 K. For the temperature range below 700 K, $K_{\text{eq,smr}} \ll 1$ and $K_{\text{eq,wgs}} > 1$ which suggests $X_{\text{CH}_4} \ll 1$ and also $X_{\text{CH}_4} \sim X_{\text{CO}_2}$. Therefore, the eqs. (13) and (19) can be simplified:

$$K_{\text{eq,wgs}} = \frac{(4X_{\text{CH}_4})^3}{(1 - X_{\text{CH}_4})(\beta - 2X_{\text{CH}_4})(1 + 2X_{\text{CH}_4} + \beta)^2} \quad (20)$$

$$K_{\text{eq,wgs}} = \frac{(4X_{\text{CH}_4})(X_{\text{CH}_4})}{(\beta - 2X_{\text{CH}_4})} \quad (21)$$

If we multiply eq. (20) and eq. (21), let $X_{\text{CH}_4} \ll 1$ and $\beta = 1$ then we obtain:

$$K_{\text{eq,smr}} \cdot K_{\text{eq,wgs}} = 64 \cdot X_{\text{CH}_4}^5 \quad (22)$$

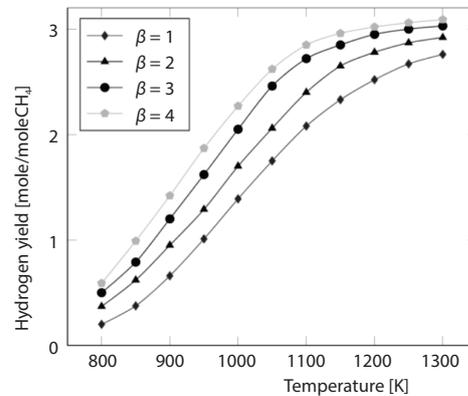


Figure 4. Hydrogen yield for the various β ratio at $p = 10$ bar

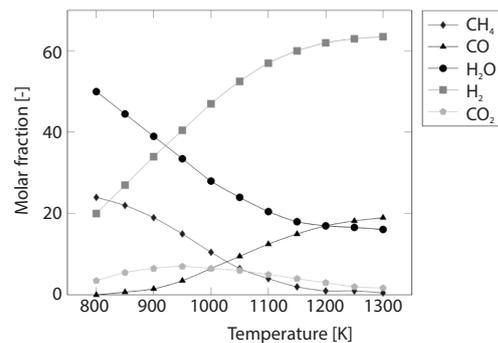


Figure 5. The equilibrium gas composition for $\beta = 2$ (solid line) at $p = 10$ bar

For the temperature range above 1200 K, $K_{eq,smr} \gg 1$ and $K_{eq,wgs} \ll 1$ which suggests $X_{CH_4} \sim 1$ and also $X_{CO_2} \sim 0$. Therefore, the eqs. (13) and (19) can be simplified:

$$K_{eq,wgs} = \frac{(3X_{CH_4}^3)(X_{CH_4})}{(1-X_{CH_4})(\beta-X_{CH_4})(1+2X_{CH_4}+\beta)^2} \quad (23)$$

$$K_{eq,wgs} = \frac{(3X_{CH_4})}{(X_{CH_4})(\beta-X_{CH_4})} \quad (24)$$

If we multiply eqs. (23) and (24), let $X_{CH_4} \sim 1$ and $\beta = 1$ then we obtain:

$$K_{eq,smr} \cdot K_{eq,wgs} = 4.5 \frac{X_{CH_4}^4}{(1-X_{CH_4})(1-X_{CH_4}^2)} \quad (25)$$

Carbon formation

Carbon formation is another factor that needs to be considered by thermodynamic analysis. For many publications devoted to thermodynamic analysis of the steam methane reforming process, the carbon formation was omitted. We can predict favorable conditions for carbon formation more accurately by utilizing the developed algorithm. From the analysis of the chemical equations shown in tab. 1, it is seen that in order to prevent the carbon formation, the following conditions must be fulfilled:

- for temperature above ~ 950 K:

$$\frac{P_{H_2}^2}{P_{CH_4}} > K_{eq,4}, \quad \frac{P_{CO_2}}{P_{CO}^2} > K_{eq,5} \quad (26)$$

- for temperature below ~ 950 K:

$$\frac{P_{CO} \cdot P_{H_2}}{P_{H_2O}} < K_{eq,6}, \quad \frac{P_{CO_2} \cdot P_{H_2}^2}{P_{H_2O}^2} < K_{eq,7} \quad (27)$$

where i -index for the equilibrium constants $K_{eq,i}$ is number of reaction in tab. 1.

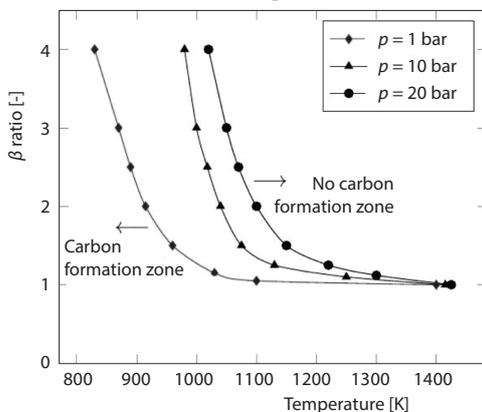


Figure 6. The operational conditions for the probable carbon formation in the steam methane reforming process

To determine the equilibrium composition we must write the material balance equation and the law mass equation for the temperature range above ~ 950 K and below ~ 950 K as it was shown previously. For equation system with seven equations we will have six variables: $\dot{n}_{CH_4,2}$, $\dot{n}_{CO_2,2}$, $\dot{n}_{H_2,2}$, $\dot{n}_{H_2O,2}$, $\dot{n}_{CO,2}$, and β . A system of equations consisting of the equations of material balance and the law mass equation can be solved by any numerical method. An iterative method of successive approximations was used for this equation system.

Figure 6. depicts the minimum temperature for the various β ratio at which the steam methane reformer can operate without having

carbon formation in the reaction zone. Conditions (area in fig. 6) to the left of the curve for various pressures show the zone at which carbon formation is favored. Temperature ranges to the right of each graph for a constant steam-to-methane ratio means operating on an area where carbon formation is not favored. Figure 6 shows that with increasing pressure, the carbon formation zone decreases. That is why for the large-scale hydrogen production by the steam methane reforming process, the pressure is above 10 bar [2].

Heat balance

To determine the required heat for the steam methane reforming process, it is necessary to write the heat balance equation for the chemical system presented in fig. 1. The heat balance equation makes it possible to determine the amount of heat supplied per 1 mole of CH₄ fed to the reformer to achieve a targeted degree of CH₄ conversion. In general, the energy balance equation for a chemical-technological system in which work is not produced (not consumed) takes the form:

$$\dot{Q} = - \sum_{i=1}^l \dot{n}_{i,j} H_i^{T_j} \quad (28)$$

where \dot{Q} [Js⁻¹] is the rate of energy input to the reformer, $H_i^{T_j}$ [Jmol⁻¹] – the molar enthalpy of the i^{th} element at a temperature of $T_j K$, and l – the total number of inlets and outlets, the flows to the reformer is considered as positive, the flows from the reformer are negative. For further analysis at the reformer inlet $j = 1$, at the reformer outlet $j = 2$.

Therefore, the heat balance equation for the reformer in fig. 1 can be written:

$$\begin{aligned} \dot{Q} = & \dot{n}_{\text{H}_2,2} \cdot H_{\text{H}_2}^{T_2} + \dot{n}_{\text{CO}_2,2} \cdot H_{\text{CO}_2}^{T_2} + \dot{n}_{\text{CO}_2,2} \cdot H_{\text{CO}_2}^{T_2} + \dot{n}_{\text{CH}_4,2} \cdot H_{\text{CH}_4}^{T_2} + \\ & + \dot{n}_{\text{H}_2\text{O},2} \cdot H_{\text{H}_2\text{O}}^{T_2} - \dot{n}_{\text{H}_2\text{O},1} \cdot H_{\text{H}_2\text{O}}^{T_1} - \dot{n}_{\text{CH}_4,1} \cdot H_{\text{CH}_4}^{T_1} \end{aligned} \quad (29)$$

Using eqs. (6)-(11), we can obtain the energy balance equation:

$$\begin{aligned} \dot{Q} = & \dot{n}_{\text{CH}_4,1} (3X_{\text{CH}_4} + X_{\text{CO}_2}) H_{\text{H}_2}^{T_2} + \dot{n}_{\text{CH}_4,1} (1 - X_{\text{CH}_4}) H_{\text{CH}_4}^{T_2} + \\ & + \dot{n}_{\text{CH}_4,1} (X_{\text{CH}_4} - X_{\text{CO}_2}) H_{\text{CO}_2}^{T_2} + \dot{n}_{\text{CH}_4,1} (\beta - X_{\text{CH}_4} - X_{\text{CO}_2}) H_{\text{H}_2\text{O}}^{T_2} + \\ & + \dot{n}_{\text{CH}_4,1} (X_{\text{CO}_2}) H_{\text{CO}_2}^{T_2} - \dot{n}_{\text{CH}_4,1} \cdot H_{\text{CH}_4}^{T_1} - \dot{n}_{\text{CH}_4,1} \cdot \beta \cdot H_{\text{H}_2\text{O}}^{T_1} \end{aligned} \quad (30)$$

The eq. (30) can be grouped:

$$\begin{aligned} \dot{Q} = & \dot{n}_{\text{CH}_4,1} \left[X_{\text{CH}_4} (H_{\text{H}_2}^{T_2} + H_{\text{CO}_2}^{T_2} - H_{\text{CH}_4}^{T_2} - H_{\text{H}_2\text{O}}^{T_2}) + X_{\text{CO}_2} (H_{\text{H}_2}^{T_2} + H_{\text{CO}_2}^{T_2} - H_{\text{CO}_2}^{T_2} - H_{\text{H}_2\text{O}}^{T_2}) + \right. \\ & \left. + (H_{\text{CH}_4}^{T_2} - H_{\text{CH}_4}^{T_1}) + \beta (H_{\text{H}_2\text{O}}^{T_2} - H_{\text{H}_2\text{O}}^{T_1}) \right] \end{aligned} \quad (31)$$

and eq. (31) simplified:

$$\dot{Q} = \dot{n}_{\text{CH}_4,1} \left[(H_{\text{CH}_4}^{T_2} - H_{\text{CH}_4}^{T_1}) + \beta (H_{\text{H}_2\text{O}}^{T_2} - H_{\text{H}_2\text{O}}^{T_1}) + X_{\text{CH}_4} (H_{\text{smr}}) + X_{\text{CO}_2} (H_{\text{wgs}}) \right] \quad (32)$$

where H_{smr} and H_{wgs} is the enthalpy of steam methane reforming reaction and water-gas shift reaction, 1 and 2 according to tab. 1.

The eq. (32) has a clear physical meaning where it is showing that the resulting transformation of substances in the steam methane reformer can be presented as a sequential heating of the feed streams of CH₄ (\dot{n}_{CH_4}) and steam ($\beta \dot{n}_{\text{CH}_4}$) from the inlet temperature T_1 to the out-

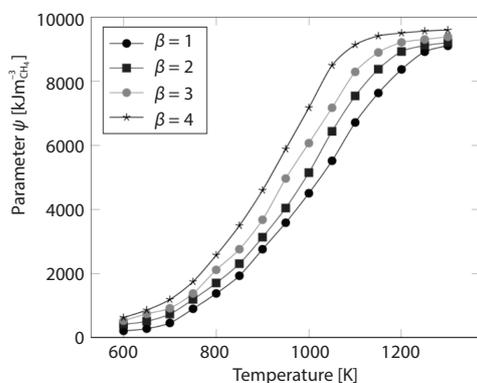


Figure 7. The heat amount supplied per 1 m³ (under n.c.) of CH₄ entering the reformer for the equilibrium CH₄ conversion for the various β ratio at $p = 10$ bar

reaction 17 mixture, then the amount of heat supplied for 1 m³ of CH₄ increases. This is due to the fact that some of the heat is expended on steam heating from T_1 to T_2 , according to eq. (32).

Conclusions

In this article, a thermodynamic analysis of the steam methane reforming is conducted in a wide range of operational conditions such as temperature, pressure, and the inlet steam-to-methane ratio. The calculations were carried out at thermodynamic equilibrium conditions via a conjugate solution of the material balance equations and the mass action law equations. For this goal the material balance equations were obtained for all elements of the reformat (product) gas. The composition of the outlet products was expressed using parameters β , X_{CH_4} , and X_{CO_2} . The algorithm for determination of the degree of CH₄ conversion and the CH₄ conversion CO₂ were presented. The results of thermodynamic analysis were compared with the results obtained via the different commercial and open-source programs such as Aspen HYSYS, IVTANTHERMO, and Chemkin. All of these results are in excellent agreement. With help of developed algorithms, the operational conditions of the carbon formation were determined. It was established that for the temperature range above 1100 K, the probability of carbon formation is absent for steam-to-methane ratios above unit. Moreover, it was determined that with increasing pressure at the temperature range below 1100 K, the carbon formation zone decreases. That is why for the large-scale hydrogen production by the steam methane reforming process, the pressure is above 10 bar. The heat balance equation for the steam methane reformer was written to determine the amount of heat supplied per 1 mole (m³ under n.c.) to the reformer in order to achieve a targeted degree of CH₄ conversion. For this purpose, a parameter ψ was used. It was found that with an increase in the temperature, the amount of heat necessary to obtain an equilibrium degree of CH₄ conversion increases. The obtained heat balance equation shows that the resulting transformation of substances in the steam methane reformer can be presented as a sequential heating of the feed streams of CH₄ ($\dot{n}_{\text{CH}_4,1}$) and steam ($\beta\dot{n}_{\text{CH}_4}$) from the inlet temperature T_1 to the outlet temperature T_2 , the taking place of steam methane reforming reaction at the temperature T_2 , the transformation of the part of the produced CO via the water-gas shift reaction at the temperature T_2 .

let temperature T_2 , the taking place of the steam methane reforming reaction at the temperature T_2 , the transformation of the part of the produced CO via the water-gas shift reaction at the temperature T_2 .

The eq. (33), taking into account the equations of the material balance, allows calculating the required heat flux to reach a targeted degree of CH₄ conversion, which is less than or equal to the equilibrium value for any combination of parameters β , p , T_1 , and T_2 .

Figure 7 shows the dependence of ψ parameter as a function on the temperature for various steam-to-methane ratio at $p = 10$ bar. The inlet temperature is 600 K. As it can be seen from fig. 7, if the amount of steam increases in the inlet

Acknowledgment

This study was financially supported by the Russian Science Foundation (project 19-19-00327).

Nomenclature

ΔG° – Gibbs energy, [kJmol⁻¹]
 $H_i^{T_j}$ – molar enthalpy of the i^{th} element at a temperature of T_j , [Jmol⁻¹]
 H_{smr} – enthalpy of steam methane reforming reaction, [Jmol⁻¹]
 H_{wgs} – enthalpy water-gas shift reaction, [Jmol⁻¹]
 $K_{\text{eq}(i)}$ – equilibrium constant of i -reaction, [-]
 $K_{\text{eq,wgs}}$ – equilibrium constant for water-gas, [-]
 $K_{\text{eq,smr}}$ – equilibrium composition for steam methane reforming reaction, [-]
 l – total number of inlets and outlets, [-]
 $\dot{n}_{i,j}$ – molar flow rate of i -element through j inlet (or outlet), [mols⁻¹]
 p – total pressure in the reformer, [bar]
 \dot{Q} – rate of energy input to the reformer, [Js⁻¹]

R – gas constant, [J(mol·K)⁻¹]
 T – temperature, [K]
 X_{CH_4} – CH₄ conversion degree, [-]
 X_{CO_2} – degree of CH₄ conversion CO₂, [-]

Greek symbols

β – parameter determining the composition of the gas mixture at the inlet, [-]
 ψ – heat amount supplied per 1 mole of CH₄ entering the reformer, [kJm⁻³]

Subscripts

eq,wgs – equilibrium compositions for water-gas
eq,smr – equilibrium composition for steam methane

References

- [1] Diglio, G., *et al.*, Techno-Economic Analysis of Sorption-Enhanced Steam Methane Reforming in a Fixed Bed Reactor Network Integrated with Fuel Cell, *Journal of Power Sources*, 364 (2017), Oct., pp. 41-51
- [2] Tran, A., *et al.*, The CFD Modelling of a Industrial-Scale Steam Methane Reforming Furnace, *Chemical Engineering Science*, 171 (2017), Nov., pp. 576-598
- [3] Nobandegani, M. S., *et al.*, An Industrial Steam Methane Reformer Optimization Using Response Surface Methodology, *Journal of Natural Gas Science and Engineering*, 36 (2016), Part A, pp. 540-549
- [4] Taji, M., *et al.*, Real Time Optimization of Steam Reforming of Methane in an Industrial Hydrogen Plant, *International Journal of Hydrogen Energy*, 43 (2018), 29, pp. 13110-13121
- [5] Pashchenko, D., Effect of the Geometric Dimensionality of Computational domain on the Results of CFD-Modelling of Steam Methane Reforming, *International Journal of Hydrogen Energy*, 43 (2018), 18, pp. 8662-8673
- [6] Chen, J., *et al.*, Computational Fluid Dynamics Modelling of the Millisecond Methane Steam Reforming in Micro-Channel Reactors for Hydrogen Production, *RSC Advances*, 8 (2018), 44, pp. 25183-25200
- [7] Inbamrung, P., *et al.*, Modelling of a Square Channel Monolith Reactor for Methane Steam Reforming, *Energy*, 152 (2018), June, pp. 383-400
- [8] Shin, G., *et al.*, Thermal Design of Methane Steam Reformer with Low-Temperature Non-Reactive Heat Source for High Efficiency Engine-Hybrid Stationary Fuel Cell System, *International Journal of Hydrogen Energy*, 42 (2017), 21, pp. 14697-14707
- [9] Lei, L., *et al.*, Thermodynamic and Experimental Assessment of Proton Conducting Solid Oxide Fuel Cells with Internal Methane Steam Reforming, *Applied Energy*, 224 (2018), Aug., pp. 280-288
- [10] Wang, B., *et al.*, A Theoretical Framework for Multiphysics Modelling of Methane Fueled Solid Oxide Fuel Cell and Analysis of Low Steam Methane Reforming Kinetics, *Applied Energy*, 176 (2016), Aug., pp. 1-11
- [11] Pashchenko, D., Combined Methane Reforming with a Mixture of Methane Combustion Products and Steam over a Ni-Based Catalyst: An Experimental and Thermodynamic Study, *Energy*, 185 (2019), Oct., pp. 573-584
- [12] Pashchenko, D., Energy Optimization Analysis of a Thermochemical Exhaust Gas Recuperation System of a Gas Turbine Unit, *Energy Conversion and Management*, 171 (2018), Sept., pp. 917-924
- [13] Pashchenko, D., First Law Energy Analysis of Thermochemical Waste-Heat Recuperation by Steam Methane Reforming, *Energy*, 143 (2018), Jan., pp. 478-487
- [14] Pashchenko, D., *et al.*, Comparison Study of Thermochemical Waste-Heat Recuperation by Steam Reforming of Liquid Biofuels, *International Journal of Hydrogen Energy*, 45 (2020), 7, pp. 4174-4181

- [15] Olmsted, G. P., Heat Engine Efficiency Enhancement-through Chemical Recovery of Waste Heat, *Proceedings, 7th Intersociety Energy Conversion Engg. Con.*, Washington D.C., 1972, pp. 241-248
- [16] Gaber, C., *et al.*, An Experimental Study of a Thermochemical Regeneration Waste Heat Recovery Process Using a Reformer Unit, *Energy*, 155 (2018), July, pp. 381-391
- [17] Lutz, A. E., *et al.*, Thermodynamic Analysis of Hydrogen Production by Steam Reforming, *International Journal of Hydrogen Energy*, 28 (2003), 2, pp. 159-167
- [18] Pashchenko, D., Thermodynamic Equilibrium Analysis of Combined Dry and Steam Reforming of Propane for Thermochemical Waste-Heat Recuperation, *International Journal of Hydrogen Energy*, 42 (2017), 22, pp. 14926-14935
- [19] Ozkara-Aydinoglu, S., Thermodynamic Equilibrium Analysis of Combined Carbon Dioxide Reforming with Steam Reforming of Methane to Synthesis Gas, *International Journal of Hydrogen Energy*, 35 (2010), 23, pp. 12821-12828
- [20] Xu, J., Froment, G. F., Methane Steam Reforming, Methanation and Watergas Shift: I. Intrinsic Kinetics, *AIChE Journal*, 35 (1989), 1, pp. 88-96
- [21] Hou, K., Hughes, R., The Kinetics of Methane Steam Reforming over a Ni/ α -Al₂O₃ Catalyst, *Chemical Engineering Journal*, 82 (2001), 1, pp. 311-328
- [22] Wang, H., *et al.*, Steam Methane Reforming on a Ni-Based Bimetallic Catalyst: Density Functional Theory and Experimental Studies of the Catalytic Consequence of Surface Alloying of Ni with Ag, *Catalysis Science & Technology*, 7 (2017), 8, pp. 1713-1725
- [23] Yoon, Y., *et al.*, Enhanced Catalytic Behavior of Ni Alloys in Steam Methane Reforming, *Journal of Power Sources*, 359 (2017), Aug., pp. 450-457
- [24] Watanabe, F., *et al.*, Influence of Nitrogen Impurity for Steam Methane Reforming over Noble Metal Catalysts, *Fuel Processing Technology*, 152 (2016), Nov., pp. 1-21
- [25] Kumar, A., *et al.*, A Physics-Based Model for Industrial Steam-Methane Reformer Optimization with Non-Uniform Temperature Field, *Computers & Chemical Engineering*, 105 (2017), Oct., pp. 224-236
- [26] Herce, C., *et al.*, Computationally Efficient CFD Model for Scale-up of Bubbling Fluidized Bed Reactors Applied to Sorption-Enhanced Steam Methane Reforming, *Fuel Processing Technology*, 167 (2017), Dec., pp. 747-761
- [27] Jeong, A., *et al.*, Effectiveness Factor Correlations from Simulations of Washcoat Nickel Catalyst Layers for Small-Scale Steam Methane Reforming Applications, *International Journal of Hydrogen Energy*, 43 (2018), 32, pp. 15398-15411
- [28] Settar, A., *et al.*, Effect of Inert Metal Foam Matrices on Hydrogen Production Intensification of Methane Steam Reforming Process in Wall-Coated Reformer, *International Journal of Hydrogen Energy*, 43 (2018), 27, pp. 12386-12397
- [29] Simpson, A. P., Lutz, A. E., Exergy Analysis of Hydrogen Production Via Steam Methane Reforming, *International Journal of Hydrogen Energy*, 32 (2007), 18, pp. 4811-4820
- [30] Rosen, M., Thermodynamic Investigation of Hydrogen Production by Steammethane Reforming, *International Journal of Hydrogen Energy*, 16 (1991), 3, pp. 207-217
- [31] Belov, G. V., *et al.*, Ivtanthermo for Windows Database on Thermodynamic Properties and Related Software, *Calphad*, 23 (1999), 2, pp. 173-180
- [32] Gurvich, L., *et al.*, *IVTANTHERMO-A Thermodynamic Database and Software System for the Personal Computer*, NIST Special Database 5, CRC Press, Boca Raton, Fla., USA, 1993
- [33] Wang, H., *et al.*, Thermodynamic Analysis of Hydrogen Production from Glycerol Autothermal Reforming, *International Journal of Hydrogen Energy*, 34 (2009), 14 pp. 5683-5690
- [34] Pashchenko, D., Thermochemical Recovery of Heat Contained in Flue Gases by Means of Bioethanol Conversion, *Thermal Engineering*, 60 (2013), 6, pp. 438-443
- [35] Sun, Y., *et al.*, Thermodynamic Analysis of Mixed and Dry Reforming of Methane for Solar Thermal Applications, *Journal of Natural Gas Chemistry*, 20 (2011), 6, pp. 568-576