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Thermodynamic analysis of thermochemical recuperation of high-temperature flue gas heat

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Abstract. The method of thermochemical recuperation of high-temperature flue gas heat by combined steam-dry methane reforming is considered. Thermodynamic analysis of the process of methane reforming with a mixture of carbon dioxide and steam is carried out using the Gibbs energy minimization method to determine the effect of operational parameters such as temperature, pressure and composition of the initial mixture on reaction products. Calculations are performed for different compositions of the initial gas mixture at a total pressure of 0.1 to 2.0 MPa, temperatures from 200 to 1200 °C. It is shown that the equilibrium concentration of methane reforming products depends only on the temperature, pressure and composition of the initial reaction mixture, and is independent of the chemical reactions that occur. The thermodynamic analysis is performed using the simulation system of stationary and non-stationary technological processes of oil and gas processing ASPEN-HYSYS.

1. Introduction

It is an interest for a large number of high-temperature heat engineering facilities to recover the heat of flue gases by the thermochemical principles of energy transformation [1-3]. The main concept of thermochemical waste-heat recuperation (TCR) is transformation of flue gases heat into chemical energy of a new synthetic fuel that has higher calorimetric properties such as low heating value. If in the conventional fuel-consuming equipment, for example the industrial furnaces, conversion of chemical energy of fuel into heat energy occurs by fuel combustion, then in the industrial furnaces with TCR the conversion of chemical energy of fuel is divided into two stages. The first stage is the increasing of the low heat value of initial propane by transformation of enthalpy waste-heat into chemical energy of the new synthetic fuel. The second stage is combustion of the new synthetic fuel that has low heat value greater than the low heat value of initial fuel. In principle, endothermic processing of any organic fuel for these purposes is possible, but its advantages and feasibility are most obvious when using natural gas consisting of 90–98% of methane.

One of the promising way of thermochemical heat recovery is a scheme in which combustion products containing steam and carbon dioxide are used as the oxidizing agent for the preliminary endothermal processing of primary fuel (reforming) [4–7]. This scheme is based on the processes of methane reforming (1) – (2) by products of its complete combustion, containing steam and carbon dioxide. Reactions (1) – (2) are accompanied by the water gas shift reaction (3).

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3\text{H}_2 - 206,1\text{ kJ/mol,} \\
\text{CH}_4 + \text{CO}_2 & = 2\text{CO} + 2\text{H}_2 - 247,3\text{ kJ/mol,} \\
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 + 41,1\text{ kJ/mol.}
\end{align*}
\]
The study of the process of steam-dry methane reforming in recent years has mainly focused on studying the characteristics of various catalysts. The dependences of the influence of temperature, pressure and composition of the initial mixture on the conversion process obtained in these studies are highly divergent due to the use of catalysts of different structures. To determine the limiting values of the influence of technological parameters (temperature, pressure, composition of the initial mixture), it is necessary to perform thermodynamic analysis. In recent years, thermodynamic equilibrium analysis of methane reforming by the Gibbs energy minimization method has been carried out by various researchers [8–10]. However, in the course of the literature and information review on the topic of the study, the results of the thermodynamic analysis of the steam-dry methane reforming were not found, in which the influence of the temperature, pressure, and composition of the initial mixture on the equilibrium composition of the conversion products was shown.

In this article, a thermodynamic analysis of the steam-dry methane reforming is carried out. The effect of pressure, composition of the initial reaction mixture and temperature on the reaction products is investigated by minimizing the Gibbs free energy in the modeling system such as ASPEN-HYSYS.

2. Methodology
The main goal of thermodynamic analysis is a determining the equilibrium composition of a particular system at certain technological parameters: temperature, pressure, composition of the initial mixture [7-10]. The equilibrium configuration of the system is determined by minimizing the Gibbs free energy, which is based on the fact that the system is in a thermodynamically favorable state when its total free Gibbs energy is at a minimum value and its differential is zero at a given temperature and pressure:

$$\left( dG^f \right)_{T, p} = 0,$$

where $G^f$ – total Gibbs free energy.

The total Gibbs energy of the thermochemical recuperation system is defined as the sum of the chemical potentials of all components of the system:

$$G^f = \sum_{i=1}^{N} n_i \mu_i,$$

where $n_i$ – number of mol of i element; $\mu_i$ – chemical potential i element.

Chemical potential of i element can be determined as:

$$\mu_i = \Delta G^0_{fi} + RT \ln \left( \hat{f}_i / f_i^0 \right),$$

where $\Delta G^0_{fi}$ – standard Gibbs free energy of formation of i element; $R$ – gas constant; $T$ – temperature; $\hat{f}_i$ – fugacity of pure species i; $f_i^0$ – fugacity of pure species i at the standard state.

Using the above expressions, we determine the total free Gibbs energy of the system as a function of the temperature, pressure, and composition of the initial mixture.

$$G^f = \sum_{i=1}^{N} n_i \Delta G^0_{fi} + \sum_{i=1}^{N} n_i RT \ln \left( \frac{\hat{f}_i}{f_i^0} \right).$$

Thermodynamic analysis is performed using the system of precise modeling of oil and gas processing processes, ASPEN-HYSYS, which is a powerful application for modeling stationary and non-stationary chemical-technological systems. ASPEN-HYSYS allows to model both single-phase and multiphase flows in an equilibrium state. The Gibbs reactor in this appendix is used to calculate the composition of the conversion products in accordance with the ongoing chemical reactions, the information of which is contained in the database of ASPEN-HYSYS.

For the analysis, a Gibbs reactor is considered that satisfies the following conditions:

a) constant temperature is maintained (on account of the purposeful organization of the heat supply) over a sufficiently extended section of the reaction space adjacent to the gas outlet. It should be expected that in the reacting mixture equilibrium is established not only with respect to the rapid the water gas
shift reaction (3), but also with relatively slower reactions of steam and carbon dioxide conversion (1) - (2), the ratio of the concentrations of all the reacting components;

b) there is no heat loss through the enclosing structures;

c) there is no change in the total pressure in the reaction space along the length.

In the present study, the dependence of the degree of conversion of the initial components on the temperature (200–1200 °C) was studied for different contents of steam in the initial mixture. The effect of pressure on the equilibrium composition of the conversion products has also been studied. For systems of thermochemical regeneration of heat due to conversion of natural gas by products of its complete combustion, the absolute content of carbon dioxide practically does not change. At the same time, the concentration of steam can be changed by additional injection of steam into the reaction space of the reactor, therefore the following initial compositions are used in the analysis: CH₄/CO₂/H₂O = 1/1/1; 1/1/2; 1/1/3. Also in the work the initial composition corresponding to the content of oxidants in combustion products of coal and other carbon fuels (there are no steam) CH₄/CO₂/H₂O = 1/1/0 is considered.

In thermodynamic calculations of chemical-technological systems, consideration of the intermediate stages of the reactions does not make sense. It can be assumed that at a process temperature not exceeding 1600 K, the molecules of simple substances do not undergo dissociation into atoms, and in the reaction products free carbon and more complex hydrocarbons are not formed.

The degree of conversion of the initial components Xᵢ as well as the yield of hydrogen YₗH₂ and carbon monoxide Y_CO is determined according to the following expressions:

\[
X_{CH_4} = \frac{[CH_4]^\text{in} - [CH_4]^\text{out}}{[CH_4]^\text{in}} \times 100\% ,
\]

\[
X_{CO_2} = \frac{[CO_2]^\text{in} - [CO_2]^\text{out}}{[CO_2]^\text{in}} \times 100\% ,
\]

\[
X_{H_2O} = \frac{[H_2O]^\text{in} - [H_2O]^\text{out}}{[H_2O]^\text{in}} \times 100\% ,
\]

\[
Y_{CO} = \frac{[CO]^\text{out}}{[CO]^\text{in} + [CH_4]^\text{out}} \times 100\% ,
\]

\[
Y_{H_2} = \frac{2[H_2]^\text{out}}{4[CH_4]^\text{in} + 2[H_2O]^\text{in}} \times 100\% .
\]

3. Results and discussion

Fig. 1 shows the equilibrium degrees of conversion of methane (X_CH₄), steam (X_H₂O), carbon dioxide (X_CO₂), depending on the temperature of the process with different contents of steam in the initial mixture. In thermochemical heat regeneration systems for high-temperature flue gases, it is technically very difficult to create an overpressure in the reaction space, therefore, a pressure close to atmospheric pressure is considered for analysis. p = 0.1 MPa. As can be seen from Fig. 1, the additional injection of steam significantly affects the degree of conversion of methane and carbon dioxide. As the steam concentration in the initial mixture increases, the degree of conversion of methane significantly increases, especially in the temperature range up to 800°C. Above 1000°C, almost complete conversion of methane is observed irrespective of the steam content due to the fact that methane is completely consumed during the course of the reactions of steam and carbon dioxide conversion. In addition, negative values of the degree of conversion of carbon dioxide with an increase in the amount of steam below 600 °C indicate that the reaction of dry methane reforming (2) is suppressed by the water shift gas reaction (3). At temperatures above 600 °C there is an increasing trend of the degree of conversion of X_CO₂, t. In the reaction space, the reaction dry methane reforming begins to dominate. This is due to
the fact that for this reaction at a temperature above 600 °C the Gibbs energy change is substantially less than for the reaction of the water gas (3).

![Figure 1](image.png)

**Figure 1.** Dependence of the degree of conversion of methane (a), steam (b) and carbon dioxide (c) on temperature for different compositions of the initial reaction mixture at p=0.1 MPa.

It is also worth considering the fact that for systems of thermochemical regeneration of heat of high-temperature flue gases, an increase in the steam content in the initial reaction mixture leads to an increase in the amount of non-combustible components in the synthesis gas. In turn, this leads to a change in the calorimetric properties of the synthetic fuel, the flame propagation velocity, and the time of thermal ignition of the gas mixture (air, hydrogen, carbon monoxide) [11-12]. Determination of the optimum ratios of process parameters, such as the temperature and composition of the initial reaction mixture, for thermochemical heat recovery systems for the heat of high-temperature flue gases is the task of a separate study.

### 3.1 Effect of the composition of the initial mixture on the yield of the conversion products

The equilibrium yield of hydrogen \( Y_{H_2} \) and carbon monoxide \( Y_{CO} \), as well as the \( H_2/CO \) ratio characterizing the composition of the conversion products, are shown in Fig. 2. According to the obtained dependences, it can be concluded that the addition of steam to the initial reaction mixture is less significant for the yield of hydrogen and carbon monoxide in the temperature range up to 650-700°C. On the other hand, at a temperature above 750–800°C, the yield of \( H_2 \) and \( CO \) decreases, with an increase in the amount of steam in the initial reaction mixture. The yield of hydrogen sharply increases at low temperatures due to the occurrence of all three basic reactions (1) – (3). For example, at a temperature of 500°C, the water gas shift reaction (3) dominates the reaction space over the reactions of steam (1) and carbon dioxide reforming (2), because reaction (3) has the smallest thermodynamic potential. The change in the free Gibbs energy at 500°C for the reactions (1), (2), and (3) is 44 kJ/mol, 32 kJ/mol, respectively, 11 kJ/mol. The maximum yields of hydrogen reach in the temperature range of 700–800 °C, depending on the composition of the initial reaction mixture. This is explained by the fact
that the change in Gibbs energy for reactions (1) – (3) in this temperature range is close and the probability of occurrence of each of the three main reactions is approximately equal.

Figure 2. The equilibrium yield of hydrogen (Y_{H_2}), carbon monoxide (Y_{CO}) and H_{2}/CO ratio as a function of temperature for the various contents of initial gas mixture at $p=0.1$ MPa.

The molar ratio of H_{2}/CO in the conversion products for various process parameters is shown in Fig. 2c. H_{2}/CO ratio in the absence of water vapor in the reaction mixture increases with increasing temperature and reaches a maximum value of 1.00 in the temperature region above 1100 °C due to the shift of the equilibrium of reaction (3) to the right. However, the nature of the H_{2}/CO=f(T) dependence varies when steam is added to the reaction mixture. At temperatures below 600 °C, the high H_{2}/CO ratio is a consequence of the influence of the reaction products of the water gas shift reaction (3), while at the higher temperatures of the dominant reaction is the carbon dioxide reforming (2), whose products also contain CO. In the temperature range above 1000 °C, the composition of the conversion products tends to constant values and changes insignificantly with the temperature increase. In conclusion, it can be said that the composition of the reaction mixture has a significant effect on the molar ratio H_{2}/CO. Thus, at a temperature of 850 °C, the ratio H_{2}/CO for the composition of the initial reaction mixture CH_{4}/CO_{2}/H_{2}O = 1/1/0 is 0.97, then with an increase in the amount of water vapor, the ratio H_{2}/CO is increased to 1.47; 1.94; 2.40, respectively, for the compositions 1/1/1; 1/1/2; 1/1/3.

The calculated values of the equilibrium compositions of the conversion products are confirmed by experimental studies (Table 1) of the joint conversion of methane by carbon dioxide and steam, performed by academic Lavrov [13]. A physical experiment was carried out in a thermochemical reactor in which a state close to equilibrium was reached. To this end, the reaction space was activated by the nickel catalyst GIAP-3 (10% NiO, support-alumina) at a space velocity of about 6,000 h^{-1}. 
Table 1. The compositions of equilibrium gas mixtures (the upper values are experimental data [13], the lower values are calculated)

| Inlet mixture | Temperature, K | Composition of products, % |
|---------------|---------------|-----------------------------|
| CH₄:H₂O:CO₂=1:1:1 | 1100 | CO₂ | 6.64 | CO | 27.33 | H₂ | 52.46 | H₂O | 13.49 | CH₄ | 0.09 |
|               | 1200 | CO₂ | 6.79 | CO | 27.16 | H₂ | 52.54 | H₂O | 13.40 | CH₄ | 0.11 |
|               |       | CO₂ | 5.56 | CO | 28.44 | H₂ | 51.53 | H₂O | 14.46 | CH₄ | 0.01 |
|               |       | CO₂ | 5.72 | CO | 28.28 | H₂ | 51.68 | H₂O | 14.31 | CH₄ | 0.01 |

3.2 Effect of pressure on the reforming process

For most schemes of thermochemical recuperation of heat of high-temperature flue gases by the natural gas reforming by the products of its complete combustion, the effect of pressure is not critical. The reforming process proceeds at atmospheric pressure. However, the use of thermochemical heat recovery in combined cycle and gas turbine plants allows the creation of excess pressure in the reaction space, so the effect of pressure on the conversion process in this work has also been studied.

The effect of pressure on the process of methane reforming for fixed values of CH₄/CO₂/H₂O = 1/1/2 in the temperature range 200–1400 °C is shown in Fig. 3. The dependences obtained show a significant pressure effect on the conversion process in the temperature range 400-1200 °C, which completely agrees in the Le Chatelier principle. In the temperature range up to 400 °C and the effect of pressure on the reforming process is minimal, because the equilibrium of the reactions (1)–(3) is shifted to the left

Figure 3. The effect of pressure on the degree of conversion of methane (a) and carbon dioxide (b) for the composition of the initial reaction mixture CH₄/CO₂/H₂O = 1/1/2.

4. Conclusion

Thermodynamic analysis of the process of steam-carbon dioxide methane reforming for systems of thermochemical heat recovery of high-temperature flue gases is performed for various technological parameters: temperature, composition of the initial reaction mixture, pressure. Thermodynamic analysis is performed using the system of precise modeling of oil-gas processing processes, ASPEN-HYSYS, which is a powerful application for modeling stationary and non-stationary systems. The calculation was carried out by minimizing the Gibbs free energy. The obtained results are confirmed by experimental data and are completely consistent with the Le Chatelier principle.

The analysis made it possible to determine the conditions under which the thermochemical regeneration process becomes possible, as well as to determine the maximum possible degrees of conversion of the initial components and the yield of the conversion products. The obtained dependences make it possible to determine the effective range of technological parameters at which it becomes possible to use thermochemical heat regeneration systems for high-temperature flue gases. The efficiency of such regeneration schemes is primarily due to the degree of conversion of methane and the composition of the products of conversion, because Xₐ depends on the amount of transformed physical
heat into chemical energy, and on the composition - the calorimetric properties of synthetic fuels (conversion products).

The use of the obtained data makes it possible to make a preliminary technical and economic assessment of the effectiveness of introducing thermochemical heat regeneration schemes, bypassing the construction of complex mathematical models describing heat and mass exchange and chemical phenomena that occur in a thermochemical reactor. Determination of optimal technological parameters for the use of thermo-chemical heat regeneration schemes requires a separate comprehensive study, but even now one can say that the use of schemes of thermochemical heat regeneration is advisable in the temperature range above 700 °C, the composition of the initial reaction mixture close to the stoichiometric and atmospheric pressure.

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