

EFFICIENCY OF THE THERMOCHEMICAL HEAT RECUPERATION SYSTEMS: HEAT- AND FLOW-DYNAMIC FEATURES

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ABSTRACT

An industrial furnace with a thermochemical heat recuperation (TCR) system by steam methane reforming is considered. A method for determining the TCR systems efficiency is proposed. The methodology is based on the determination of the heat recuperation rate. A distinctive feature of the method is taking into account the work losses due to flow-dynamic drag in a packed bed of a thermochemical recuperator. The total recuperated heat and the recuperated heat in the steam generator and the reformer as well as work losses due to flow-dynamic drag are calculated. It is established that the efficiency of the TCR system depends on the methane conversion and with increasing temperature, the efficiency of the TCR system increases. It is shown that work losses due to flow-dynamic drag do not have a significant effect on the energy balance in the TCR systems. It is established that the maximum recuperation rate is for 700°C and H₂O:CH₄=2.

Keywords: Thermochemical recuperation, Heat balance, Waste-heat, Energy efficiency, Recuperation rate

1. INTRODUCTION

Energy shortage and environment pollution have drawn more and more attention from all over the world. Estimations from International Energy Agency indicate that natural gas will be as one of the most commonly used fuel for heat-power and heat-technology units in 21st century. Today, natural gas supplies 22% of the energy used worldwide, and makes up nearly a quarter of electricity generation, as well as playing a crucial role as a feedstock for industry. Despite

great progress in the efficient use of natural gas in the heat-power and heat-technology systems, there is still a great potential for increasing energy efficiency of such systems.

There are two main ways to improve the fuel efficiency of the fuel-consuming equipment in the heat-power and heat-technology systems. The first is the rational use of traditional fuel through the improvement of fuel and technological cycles. The second is the replacement of the original fuel with alternative fuel and energy resources. A special place among alternative hydrocarbon fuels is (in view of high environmental friendliness) the so-called synthetic fuel - hydrogen-containing gas that obtained directly in the fuel-consuming system. Such technology of synthetic fuel generation is sometimes called as on-board hydrogen production [1]. One of the ways to increase energy efficiency, which satisfies the above two directions, is thermochemical waste-heat recuperation [2].

The main criterion for the effectiveness of the TCR system is the heat recuperation rate of exhaust heat. The recuperation rate shows how much the exhaust heat is usefully returned to the fuel cycle in relation to the total exhaust heat. In addition, it is known that in the thermochemical recuperation systems the main element is a thermochemical recuperator. The thermochemical recuperator is a heat exchanger with a fixed-bed. The fixed bed is filled with various catalysts. The most commonly used catalyst is a nickel-based catalyst. The outstanding feature of such thermochemical recuperators is a high pressure drop in a fixed bed.

The main goal of the presented paper is the development and scientific justification of a universal method for determining the heat recuperation rate of

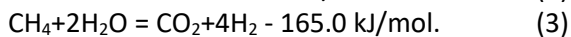
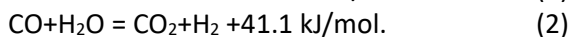
the exhaust heat in the TCR systems taking into account a pressure drop in the thermochemical recuperators. In addition, based on the developed method and previous author's experimental studies, it is necessary to determine the recuperation rate for the TCR system by steam methane reforming with taking into account a pressure drop in the thermochemical recuperators.

2. TCR CONCEPT

The general idea of thermochemical recuperation is to use the exhaust heat for fuel reforming of initial fuel. As a result of this transformation, new synthetic fuel (product of fuel reforming) has higher low heat value (LHV) in comparison with LHV of initial fuel. Endothermic reactions for TCR may be different. However, steam methane reforming has the widest application for TCR.

A schematic diagram of a gas furnace with thermochemical recuperation by steam methane reforming is shown in Fig.1. The schematic diagram can be virtually divided into two blocks: (1) a thermochemical recuperation system (a methane reformer, a steam generator (boiler), a mixer (steam ejector)); (2) a fuel consuming system (fuel-consuming equipment itself, burner assembly).

In this schematic diagram, the waste flue gas after a gas furnace is sequentially passing through the methane reformer and a boiler (steam generator). The methane reformer performs as a catalytic heat exchanger. The reaction mixture before the reformer is containing steam and methane. Inside the reaction space of the reformer, methane and steam are reacted and the mixture that mainly consists of hydrogen is produced. The chemical endothermic reaction of the steam methane reforming process can be written as follows [3]:



The main criterion for the energy efficiency of the heat recuperation system is the recuperation rate $\text{\cite{zhang2013review,soylemez2000optimum}}$. The heat recuperation rate shows how much heat of the exhaust gases is recovered in the fuel cycle of a gas furnace. Obviously, the efficiency of using the TCR systems is determined by the conversion of original fuel (degree of methane conversion). If the reforming reaction does not proceed, the efficiency of the TCR system is zero. On the other hand, the methane conversion depends on operating temperature,

pressure and methane/steam feed composition, and the reformer characteristics [4]. Therefore, the heat recuperation rate depends on operating conditions and

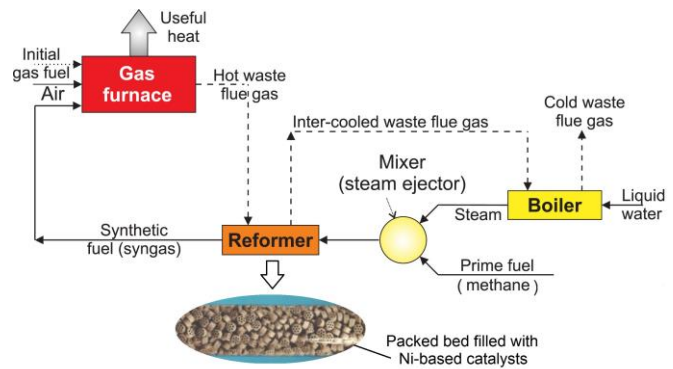


Fig 1 Schematic view a gas furnace with thermochemical recuperation by steam methane reforming

the design characteristics of the reformer.

In addition, to determine the real efficiency of the use of TCR systems, it is necessary to take into account the work losses due to flow-dynamic drag of the catalyst bed. If in the traditional recuperators for air preheating such losses is only a few dozen Pascal, then in the thermochemical recuperators pressure loss is 3000-5000 Pascal.

3. METHODOLOGY

The efficiency of application the TCR systems by steam methane reforming is depending on the heat transferred in the reformer for the methane reforming reaction and syngas heating. If steam methane reforming doesn't occur in the reformer, then the efficiency of using of the TCR system equals to zero or even has a negative effect, due to the fact that exhaust heat is used for generation of steam. In addition, an increasing steam-to-methane ratio in feed stream leads to an increase of mole fraction of non-combustible species in syngas, in particular steam. Residual steam and carbon dioxide (produced by water-gas shift reaction) are the components of syngas but from the energy point of view, residual steam and CO_2 doesn't play a positive role in the combustion process, because H_2O and CO_2 is non-combustible inert material of synfuel. Moreover, a large amount of heat is required for steam generation and from an energy point of view, a large molar fraction of steam in synfuel is negative [5]. Therefore, determining the optimal steam-to-methane ratio in the TCR system is an important engineering task.

According to the definition, the heat recuperation rate can be expressed as follows:

$$R = \frac{H_{rec}}{H_{exh}} = \frac{H_{rec}^{ref} + H_{rec}^{st.gen}}{H_{exh}}, \quad (4)$$

where H_{rec} - a recovered heat in the TCR system, kJ; H_{rec}^{ref} , $H_{rec}^{st.gen}$ - a recovered heat in a reformer and a steam generator, respectively, kJ; H_{exh} - an exhaust heat after a furnace, kJ.

If we assume that the energy loss due to flow-dynamic drag is the expenditure part of the energy balance, then expression (4) will have the following form:

$$R = \frac{H_{rec}^{ref} + H_{rec}^{st.gen} - W_{fd}^{ref}}{H_{exh}}, \quad (5)$$

where W_{fd}^{ref} - a work loss due to flow-dynamic drag in the thermochemical recuperators - reformers, kJ.

The work loss due to flow-dynamic drag depends on a pressure drop in the reformer, mass-flow rate and average density of the reaction mixture. The density of the reaction mixture along the length of the reformer varies. First, due to changes in the composition of the reaction mixture. Secondly, due to temperature and pressure changes in the reformer.

The enthalpy of the exhaust gases depends on the steam-to-methane ratio in the reformer. As the steam-to-methane ratio increases, the amount of steam in the combustion products increases.

The heat transferred to the reformer is not equal to the recovered heat because syngas consists of combustible elements (H_2 , CO , CH_4) and non-combustible elements (H_2O , CO_2). Therefore, the enthalpy of noncombustible elements in syngas can't be taken into account as a recovered heat because in this case, these elements are the inertial materials. Therefore, the recovered heat in the reformer can be calculated as follows:

$$H_{rec}^{ref} = H_{SMR} + H_{sg} - H_{H_2O} - H_{CO_2} - H_{mix}, \quad (4)$$

where H_{SMR} -- enthalpy of steam methane reforming reaction, kJ; H_{sg} - syngas enthalpy, kJ; H_{H_2O}, H_{CO_2} -- enthalpy of steam and carbon dioxide that are contained in syngas, kJ; H_{mix} - enthalpy of steam-methane mixture before the reformer, kJ.

Synthesis gas enthalpy, the enthalpy of H_2O and CO_2 in synthesis gas, as well as the reaction enthalpy depends on the reaction conditions. The composition of synthesis gas after the reformer can be determined both experimentally and theoretically. The reaction

enthalpy is difficult to directly determine. However, on the basis of thermodynamic analysis, it can be assumed that at the high temperatures, the main contribution to the material and heat balance is made by reaction (1) in comparison with the water-gas shift reaction (2). Therefore, we can assume that the reaction enthalpy is determined by a methane conversion:

$$H_{smr} \approx X_{CH_4} \cdot \Delta H_{298}^0; \quad \Delta H_{298}^0 = 206.1 \text{ kJ/mol}, \quad (6)$$

where X_{CH_4} is a methane conversion.

The heat of inter-cooled exhaust gas that transferred to steam generator also cannot be considered as a recovered heat because part of steam (if steam-to-methane ratio greater than 1 or if CH_4 conversion is less 1 for steam-to-methane ratio of 1) is containing in syngas and also don't play a role (from an energetic point of view) as a combustion component. Therefore, the recovered heat in the steam generator must be calculated as follows:

$$H_{rec}^{st.gen} = (h_{st} - c_p \cdot t_w^{in}) (G_{st}^{in} - G_{st}^{sg}), \quad (7)$$

where h_{st} - the enthalpy of steam after a steam generator, kJ; G_{st}^{in} , G_{st}^{sg} - the mass flow rate of water before a steam generator and the mass flow rate of steam in syngas, kg/s; t_w^{in} - temperature of feed water, °C; c_p is the heat capacity of feed water, kJ/(kg·°C).

The main task for determining the heat recuperation rate of the TCR systems is the determination of syngas composition after the reformer. It is known that the composition of synthesis gas depends on the operating parameters, such as temperature, pressure and composition of the feed mixture, on the residence time (contact time of reaction mixture with a catalyst), on the characteristics of the reformer such as the composition and shape of the catalyst, the size of the reaction space.

4. RESULTS AND DISCUSSION

In this paper, syngas composition and pressure drop in the reformer for calculating the heat recuperation rate is partly taken from the results of the author's previous experimental studies. The author's previous works deal with an experimental study of a methane reforming process to understand the reforming characteristics and pressure drop in the reformer [6].

Based on the previous experimental results and methodology described above, the recuperation rate of the thermochemical waste-heat recuperation system is

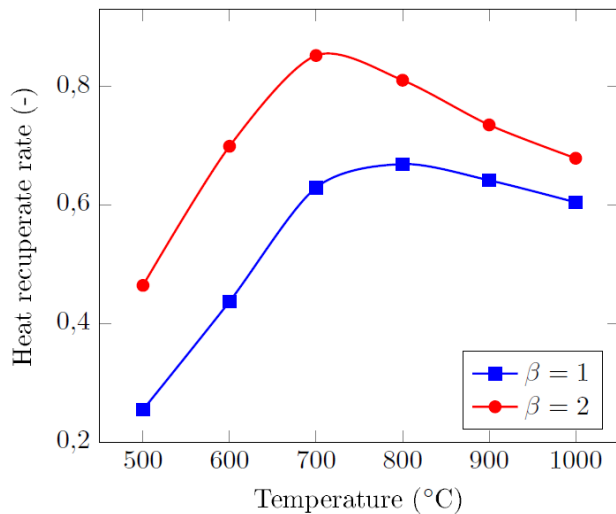


Fig 2 The heat recuperation rate of the TCR system vs. temperature of the exhaust gases

determined. Fig.2 shows the dependence of the recuperation rate on the temperature of the exhaust gases for different steam-to-methane ratios (β).

Fig.2 clearly shows that the efficiency of a TCR system greatly depends on the temperature of the exhaust gas. As mentioned above, the basic concept of the TCR systems is the transformation of the exhaust heat into the chemical energy of new synthetic fuel. The result of this transformation is the increased LHV of synfuel compared to the LHV of methane. That is why when the enthalpy of the steam reforming reaction increases, the efficiency of the TCR system increases. Fig.2 shows that the maximum heat recuperation rate takes place at 700°C and $\beta=2$.

Fig.2 makes it clear that, at a temperature of 700°C, the TCR system is capable of recovering more than 83% heat of exhaust gases after a gas furnace.

5. CONCLUSION

Based on the experimental results and the developed methodology, the following results were obtained: (1) a recovered heat increases with increasing exhaust gas temperature; in the temperature range up to 700°C, an increase in a recovered heat takes place mainly due to an increase in the enthalpy of the steam methane reforming process; (2) the heat recuperation rate for the TCR systems with a steam-to-methane ratio from 1 to 2 has a maximum value in the temperature range of 700-800°C; the maximum heat recuperation rate 0.831 is achieved at a temperature of about 700°C and a H₂O:CH₄ ratio of 2; (3) work losses due to flow-dynamic drag will not have a noticeable effect on the heat recuperation rate.

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