

The use of supercritical endothermic fuel

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Abstract. Endothermic reactions as a method of cooling are considered by many researchers due to the necessity of removal and recovery of large heat fluxes. The main applications of endothermic fuels technology are considered hypersonic aircraft. The increased interest in hydrogen energy, already implemented in specific technical developments, is pushing for consideration of existing developments not only in the spectrum of highly specialized technology of thermal protection, but also in as the hydrogen energy technology. It is proposed the use of endothermic catalytic steam reforming reaction of hydrocarbon fuel in a supercritical state. Summarizes the results achieved in detail both theoretically and experimentally investigated thermal and chemical aspects of the implementation of technology in terms of low pressure in the gaseous or liquid reagents in the light of the supercritical state of the reactants.

1. Introduction

The use as reagents of different type of hydrocarbons allows, except removal of heat by the endothermic effect of the reaction to obtain a hydrogen-containing fuel having better energy characteristics. In stand-alone hydrogen energy plants traditionally to produce hydrogen from hydrocarbon fuels regarded exothermic reaction of partial oxidation of hydrocarbons in the water vapor presence [1;2].

We have previously detailed theoretically and experimentally investigated the thermophysical and chemical aspects of the implementation of the technology in terms of low pressure in the gaseous or liquid state reagents [3;4].

2. Chemical absorption of heat

Removing heat main factors are heat capacity and the heat of phase transitions of refrigerant. A feature of the first factor is the uniform distribution of the heat capacity for heating, change in heat flow leads to a proportional increase in temperature. The second factor is different in that the heat is phase transition absorbed at a certain temperature, but for the technology used in refrigerants, these temperatures are low.

If you need to absorb large heat flows while maintaining high temperatures of cooling facilities, the best factors would be cool with a maximum heat capacity at the required temperatures usually defined by the constructional limit of the material. In addition to phase transitions of (evaporation, the transition to the supercritical state) as such may be endothermic reactions. The chemical reaction rate increases by 2-4 times temperature increases up to 10 degrees, but as the temperature change is a function of the difference between the incoming and chemically absorbed heat flux:

$$dT = f(E_{incoming} - E_{chemical\ absorbed}),$$

and absorbed heat flux is proportional to the reaction rate and, therefore, temperature::

$$E_{chemical\ absorbed} \sim V_{reaction} = f(T),$$

it balances the heat absorption heat flux increases with its growth.

3. Steam reforming, as the basis of chemical heat recovery

Developed technology of chemical heat recovery based on the steam conversion reaction of hydrocarbons [5]. Comparison of the thermal characteristics of the reaction by the example of



kerosene T1 cooling power of water, hydrogen, and thermal decomposition reaction of kerosene for different temperatures are shown in Table 1. In addition, the table shows the relative concentrations of hydrogen and carbon condensate products. Initial temperatures of all components of 393.15 K, except cryogenic hydrogen, for it is the initial temperature $T < T_{\text{boil}} = 22\text{K}$.

Table 1. Heat consumption for the cooling liquid heating and expansion, composition of the products when heated to different temperatures.

Cooling Method	$T=700\text{K}$			$T=1000\text{K}$			$T=1373,15\text{K}$		
	X H2	X carbon	ΔH kJ / kg	X H2	X carbon	ΔH kJ / kg	X H2	X carbon	ΔH kJ / kg
1 H ₂ O heat capacity boiling	0	0	3251	0	0	3910	4.24e-5	0	4818
2 T1 thermal cracking heat capacity boiling	0.09	0.52	472	0.40	0.52	3236	0.48	0,51	5415
3 43.58% T1 56.41% H ₂ O steam conversion heat capacity boiling	0.11	0.16	2246	0.51	0.08	5940	0.65	0	9258
4 H ₂ heat capacity boiling	1	0	9860	1	0	14570	1	0	20255

When heating kerosene T1, consisting of a mixture of different hydrocarbons, at a temperature of 700K in the decomposition products contained up to 9.3 mol% of hydrogen, and when to 1373.15K - up to 48 mol% H₂. Maximum heat consumption for heating a mixture of kerosene and water take place at the maximum formation of hydrogen in the product mixture. For example, at $T = 1373.15\text{ K}$ composition of 43.58% T1 and 56.41% H₂O gives the greatest amount of hydrogen in the mixture of degradation products, providing the highest heat input 9258 kJ / kg, with no soot.

Loss of heat to heat the hydrogen is much more than evaporation, heating and all other conversion of the substances. Characteristics of hydrogen are shown for comparison. The specifics of the use of hydrogen and hydrocarbon fuel are significantly different from each other, which do not allow considering them as alternative refrigerants. Thermodynamic equilibrium calculations were performed using the program, which is adaptation of the method described in [6;7], using the thermodynamic functions of the bank IVTANTHERMO [8]. Calculations were carried out for the pressure $P = 1\text{ bar}$.

The data presented in Table 1 do not reflect all the features of hydrocarbon conversion reactions as a factor in cooling. To illustrate the uneven distribution of heat absorption during the growth were calculated equilibrium compositions for a larger number of temperatures that were converted to mass fractions of the components.

When mixtures of known composition on the basis of data on the specific heat of components, taken from [8], [9] and [10], to calculate the "net" isobaric heat capacity at different temperatures. Results are presented in the form of graphs in Figure 1.

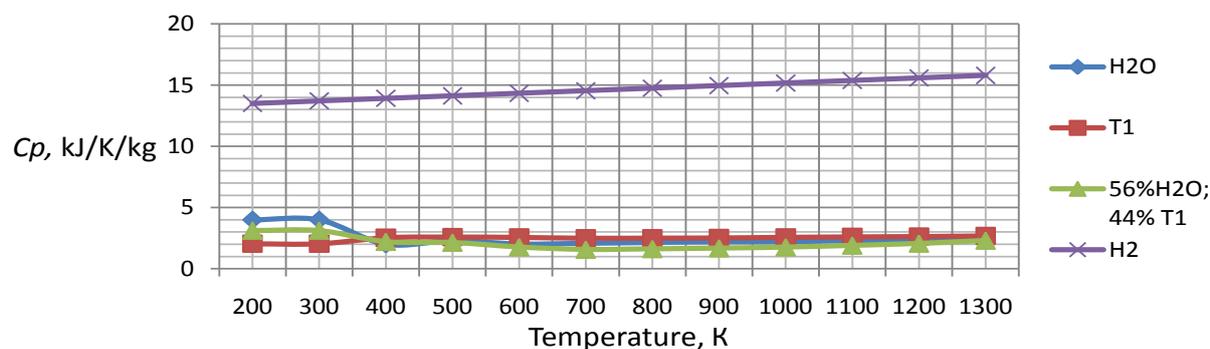


Figure 1. Refrigerant heat capacity at different temperatures.

As seen refrigerant heat much lower than that of hydrogen, even the presence in the products of the products of kerosene and steam reforming of large molar fraction of hydrogen does not improve the situation, because due to the low density of the mass fraction of hydrogen in the products is low.

To estimate the contribution to the heat-absorbing capacity of the phase transitions and chemical reactions was calculated modified indicator thermal capacity Cp' :

$$Cp'(T) = \frac{\Delta H}{\Delta T} = Cp(T) + Q_{reaction} * \frac{\Delta \alpha(T)}{\Delta T};$$

$Q_{reaction}$ – heat of chemical reaction per kg reacted; $\alpha(T)$ – conversion degree at temperature.

Since the latent heat of the phase transition is absorbed at a certain temperature, the right to display it in the same dimension that was used in Figure 1 is not possible. In order not to lose the clear presentation of the graph in dimensions kJ/K/kg of K, the latent heat of the phase transition has been allocated to the temperature range.

To estimate the contribution of the heat of the chemical reaction has been calculated changes in the equilibrium composition of refrigerant temperature increases and these changes are calculated thermal effects. The result of these operations is shown in Figure 2.

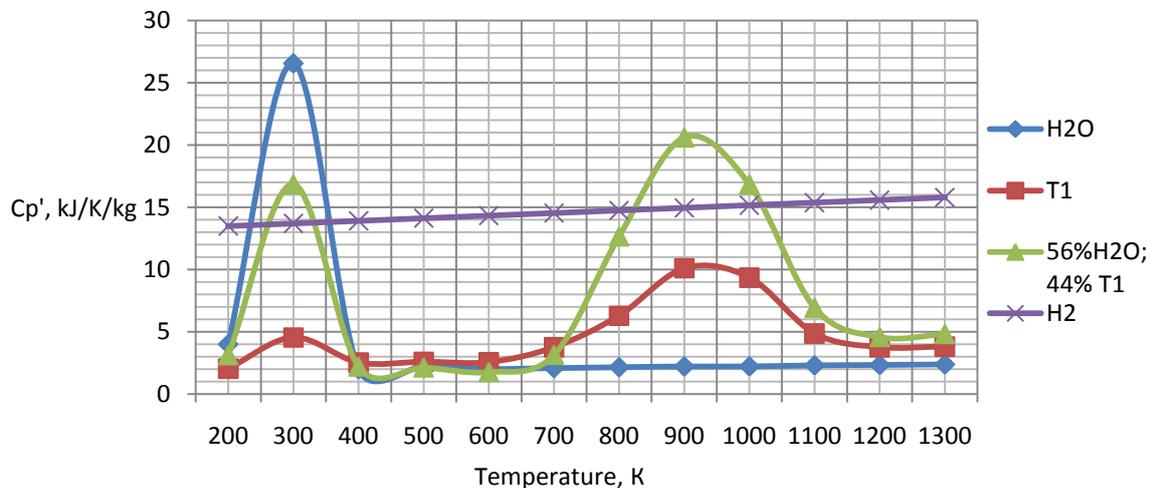


Figure 2. Modified thermal capacity indicator of refrigerants.

Thus, the use of steam reforming reaction in solving the problems has a number of features. Cooling surface temperature is maintained as close as possible to the temperature limit of heat-resistant structural materials, which has a positive impact on the flow processes stability in a refrigerated facility. High heat-absorption capacity in excess of heat-absorption capacity of hydrogen in the working area (850 K-1050 K), provides stabilization of the temperature cooled surface at this level.

4. Experimental research

This section presents the experimental results on the methane conversion at moderate heat fluxes $q \leq 100 \text{ kW/m}^2$. Schematic diagram of the setup is shown in Fig.3. The object of the pilot study is the structure of 592 mm length. A high-temperature jet of nitrogen, heating heat-transfer walls of the two slot channels was fed into the central rectangular channel of the reactor from plasmotron via adapter. Preheated mixture of hydrocarbons and water vapor was fed to the channels which actually were the reactive zone with 571 mm length, 60 mm width, and 4 mm height. It is the cooling jacket to the inner channel. The walls of TCR are made out of stainless steel used for the manufacture of flame tubes of the combustion chambers. The lengths of the reactor are 4 paired thermocouple and gas samplers. They are placed in 153 mm, 332 mm, 421 mm and 501 mm from the inlet to the reactor. 65 mm from the inlet to the reactor the single thermocouple is.

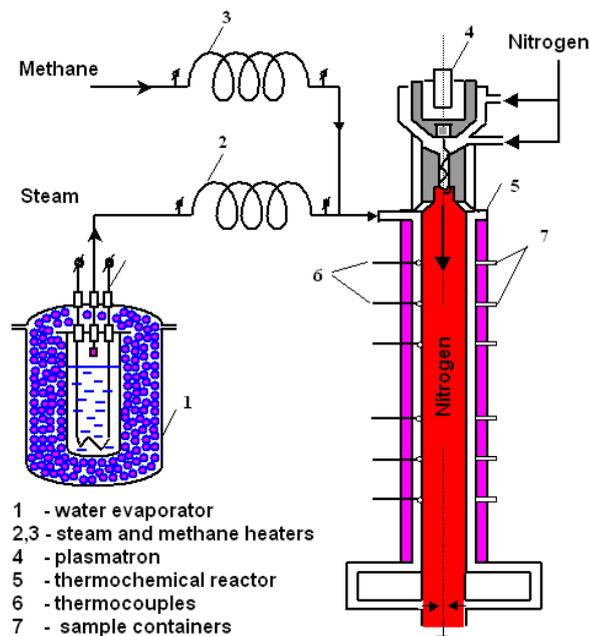


Figure 3. Experimental set-up

First, experiments were performed in the reactor with smooth walls, which have a natural catalytic activity. At flow rate of steam-methane mixture $G = 0.8 \text{ g/s}$ and a wall temperature $T_w = 1100 \text{ }^\circ\text{C}$ methane conversion degree did not exceed 6 % vol. Reduction of flow rate to 0.2 g/s resulted in the increase of conversion degree up to 37 % vol. due to the increase in the residence time of the mixture in the reactor. However, a qualitative change in the situation occurred when a volumetric nickel catalyst with a developed surface was placed into the reactor. The degree of conversion at that increased up to 92 %, as shown in Fig.4. Hydrogen yield at $G = 0.8 \text{ g/s}$ and $T_w = 1100 \text{ }^\circ\text{C}$ made up 45% vol. and at $T_w = 1300 \text{ }^\circ\text{C}$ increased up to 65 % by volume.

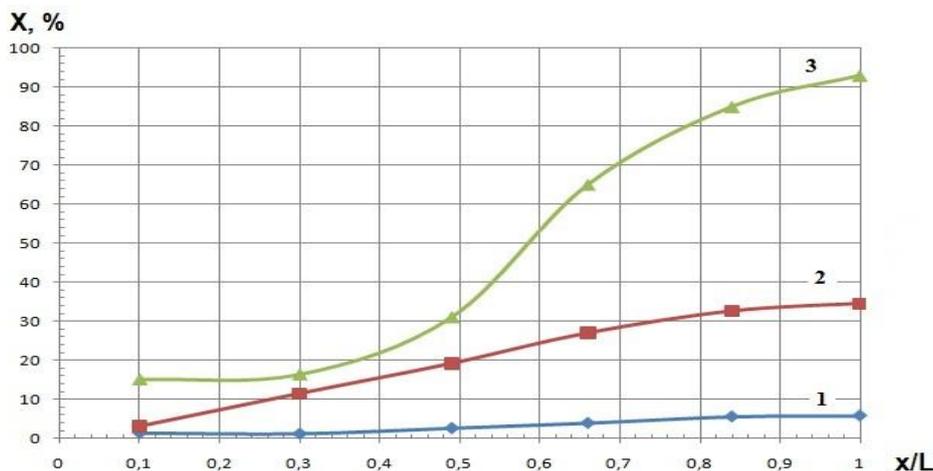


Figure 4. Steam conversion change along the reactor's length.

1 - $G = 0.8 \text{ g/s}$, smooth wall 2 - $G = 0.2 \text{ g/s}$, smooth wall 3 - $G = 0.8 \text{ g/s}$, volumetric catalyst

Our experiments qualitatively confirmed the results of calculations of TCR modeling in slender channel approximation. Flow rate of chemically reacting mixture and the temperature of the wall where the reaction takes place have the greatest effect on the characteristics of the process under study. Some patterns can be seen in the detailed consideration of the results of the third stage. Figure 5 shows the composition of the samples, as in Figure 6 the temperature of gases. Sampler 1 corresponds to thermocouple 2, sampler 2 - thermocouple 3, and so on.

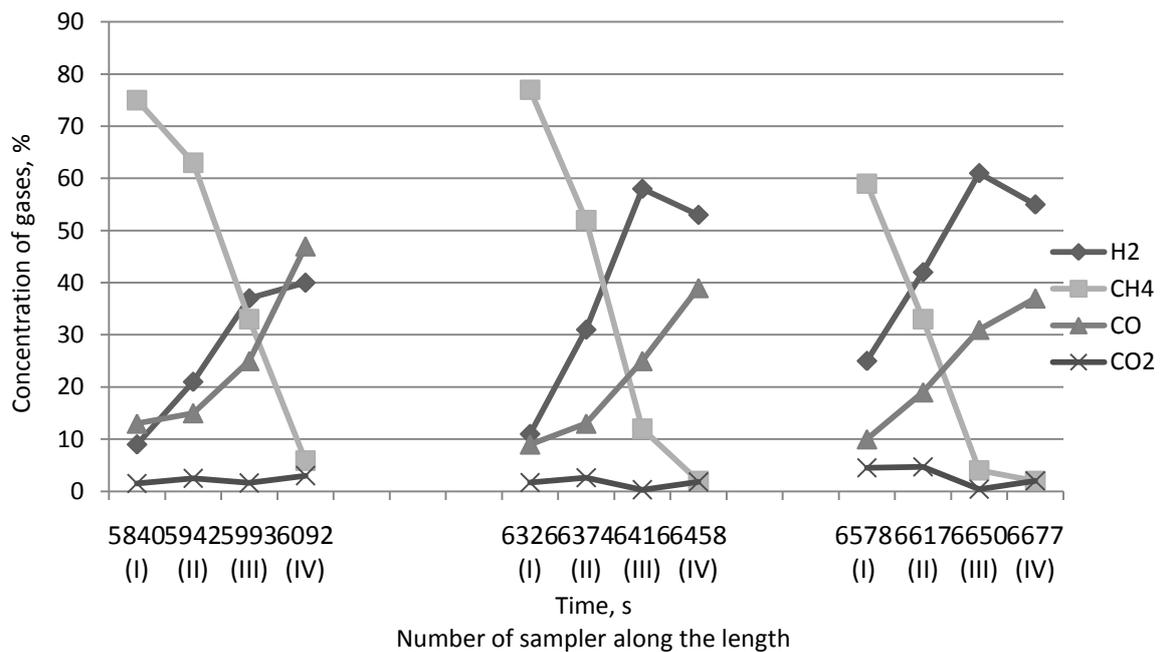


Figure 5. Gas concentration in samples.

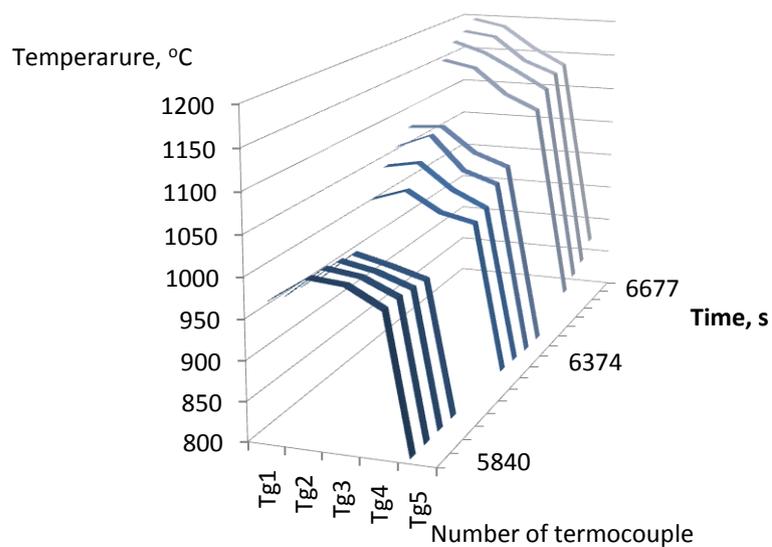


Figure 6. Gas temperature in points of sampling

The graph in Figure 5 shows that in the first mode (5840 s – 6092 s) is reached and the maximum degree of conversion of the hydrogen concentration reaches 40%. In the second (6326 s – 6458 s) and third (6578 s – 6677 s) mode, the concentration was achieved in 58% and 61% respectively. However, the drop is observed in hydrogen concentration to 53% and 55% respectively. In this case, the graph shows that the temperature at all points monotonically increasing. Accordingly, the drop is the result of the conversion course of internal processes.

Next was calculated removable heat flux and it was about 3 kW or 44 average specific kW/m³. The main reasons for the low heat flux removes include enough high heat transfer and reaction rate. Solvable problem has a dual purpose - the removal of a large heat and high conversion. For a high degree of conversion is necessary to ensure the long duration of stay in the reaction zone, since the limiting factor is the speed of the reaction, for removal of the heat flux to provide a large share of consumption and, again, the high speed of the reaction.

5. Conclusion

Obvious solution to this situation is to use a more active catalyst having a large specific surface area. But this approach several drawbacks. First, the active catalysts are expensive and mechanically weak. Secondly these catalysts are very sensitive to poisons. Thirdly, in our case is difficult to use the excess weight of the catalyst, in the case of chemical industrial plants provides long trouble free and stable operation.

As an alternative to using a larger amount of the catalyst is proposed to use an endothermic catalytic steam reforming reaction of hydrocarbon fuel in a supercritical state. Supercritical state, a separate state of aggregation, is characterized by high density and high reactivity, which distinguishes it from the gas and liquid, respectively [11]. Based on laboratory studies of hydrocarbon conversion by supercritical water [12,13], we can identify a number of advantages of this approach:

1. Separate flow conversion of hydrogen generation in the reactor heat source can use any high-temperature apparatus, in the case of the combustion chamber as a heat source; you can ensure optimal combustion in it, in contrast to the auto-thermal partial oxidation reactor, where oxidation and conversion are common.
2. Ability to raise the pressure in the reactor of hydrogen generation that the technology of the partial oxidation is difficult because of the reaction of partial oxidation sustainability and, as a consequence, the possibility of transition to a supercritical state.
3. As the density increases the residence time of reagents from the catalyst that helps intensify the reaction and reduce the size of the reactor. As a result, the limiting factor is the heat of reaction
4. Suppression of the production side products. Due to the separate reactions becomes possible to provide optimum conditions for maximum selectivity and depth conversion.
5. Formation of products of high pressure allows the use of various methods of separating the components of treatment and further storage without the cost of compression.
6. Thermal isolation is a consequence of the lack of the need for cooling, as the main target reaction is endothermic and there is no need to introduce additional refrigerant.

6. References

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