Peculiarities of hydrogen combustion in the nitrogen and water vapor media at high density of reagents

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Abstract. The paper deals with the investigation of the hydrogen combustion in mixtures of H₂/O₂/H₂O (0.70/0.35/1.64 mol L⁻¹), H₂/O₂/N₂ (0.72/0.34/1.61 mol L⁻¹), and H₂/O₂/N₂/H₂O (0.72/0.34/1.64/0.03 mol L⁻¹) under uniform heating at a rate of 1 K min⁻¹ in a tubular reactor. Based on the comparison of the time-dependent variations of the reaction mixture temperature and the temperature of the reactor wall, the self-ignition temperature is determined as well as the effect of diluent on the nature of heat release was revealed. The contributions of homogeneous and heterogeneous combustion of hydrogen and their effect on heat release in the reaction mixture are discussed. The possibility of hydrogen oxidation enhancement in the H₂O medium, associated with the involvement of vibrationally excited O₂* molecules, generated from the resonant exchange of vibrational energy with the H₂O* molecules, are considered.

1. Introduction

Supercritical water (SCW: T > 647 K, P > 22.1 MPa [1]) is characterized by low values of the ion product and dielectric constant [2]. This allows SCW to dissolve organic substances [2], and is used in the combustion of fossil fuels and organic waste directly in the heat carrier. Such combustion enhances energy efficiency and ecological cleanness of heat and electric energy production [3]. Hydrogen and methane are the main combustible products of SCW gasification of fuels and organic waste [4–6]. Combustion of methane in a nitrogen medium, saturated water vapor, and SCW in an autoclave and a flow reactor at high reagent densities was studied earlier [7]. It is shown that the temperature of methane self-ignition decreases with increasing CH₄ concentration; in the nitrogen medium methane self-ignition occurs at a temperature by 20 K higher than in the water vapor medium.

Hydrogen combustion is studied in a large number of works, some of which are considered in the review [8]. According to [8], most of the studies were carried out in the field of high temperatures (>800 K) and low pressures (<0.4 MPa). At high pressures, self-ignition of the fuel occurs at lower temperatures [7, 9, 10]. Studies of hydrogen self-ignition at high pressures (4.3–15.9 MPa) showed that addition of nitrogen to hydrogen increases the initial pressure of the mixture necessary for its self-ignition, when released into the air [11]. Mechanisms and kinetics of hydrogen combustion in SCW in flow reactor conditions at a temperature ≥773 K, pressure of 11.8–26.3 MPa, and proportion of H₂O of 99.4–99.8% mol. were investigated in [12, 13]. It is shown [13] that high density of the water increases the rate of the reaction HO₂ + H₂O → H₂O₂ + OH, which is the step of chain branching during the oxidation of hydrogen. The study [14] of hydrogen combustion kinetics in SCW in the
conditions similar to those of [12] showed a lower value of activation energy. The authors [14] explain this by the fact that in [12] the influence of the reactor wall was not fully taken into account.

Thus, the hydrogen combustion in a high-pressure water vapor at temperatures <773 K and a high density of reagents has not been studied. The aim of this work is obtaining experimental data on the self-ignition temperature and features of hydrogen combustion in a mixture of H₂/O₂/H₂O. These data are necessary for the development of safe power plants for hydrogen combustion and hydrogen-containing mixtures in SCW and understanding the mechanisms of hydrogen self-ignition. In this work, as a comparison system for H₂/O₂/H₂O, the H₂/O₂/N₂ mixture was used.

2. Experimental procedures

The tests were carried out using an experimental setup described in [7]. The main element of the setup (figure 1) is a tubular flow reactor 1 (inner diameter 30 mm, volume 65 cm³) made of stainless steel, %: 18 – Cr, 10 – Ni, 1 – Ti, the rest – Fe (analogue of AISI 321H). The volume of the reactor placed inside the furnace 2 is equal to 2 = 64.1 cm³. The inner surface of the reactor is covered with an oxide layer (whose main component is Fe₂O₄ [15]) formed as a result of oxidation with H₂O/O₂ mixture at 873 K. The furnace was heated by a resistance heater 3 and regulated by a thermocouple 4 (Tₓ) mounted on the outer surface of the reactor, and a thermal programming unit. In addition, the temperature of the reactor wall was controlled by two thermocouples 5. The temperature in the center of the reactor volume was measured by thermocouple 6 (Tₒ). The readings of Tₒ(t) and Tₓ(t) thermocouples were recorded digitally at a frequency of 10 Hz. Reagent pressure was measured by a membrane strain gauge 7 with an error of 0.25% of the measured value. The reagents were supplied to the pre-vacuumed reactor through the capillary provided with the adjusting valve 8.

In test 1 (table 1), through the rubber diaphragm 9 (figure 1), distilled water was fed into the reactor in amount of 2.8 cm³ at a room temperature through a nozzle applicator. Then the reactor was heated to Tₒ = 403 K and subjected to isothermal holding for 45 min. Part of the water (0.9 g) was condensing in the non-heated volume of the reactor, while 1.9 g (105 mmol) of H₂O remained in the heated volume of the reactor. Then, the reactor was successively fed with H₂ and O₂ (table 1).

In test 2, the reactor was successively filled with N₂, H₂, and O₂ at room temperature. In this test, the non-heated reactor volume was filled with nitrogen. In test 3, the reactor was filled with water similarly to test 1. Excess amount of water was discharged into the atmosphere at Tₒ = 403 K. As a result, the non-heated reactor volume was filled with water, while [H₂O]₀ = 1.7 mmol remained in the heated volume of the reactor (table 1). Then the reactor was filled with N₂, H₂, and O₂ similarly to test
2. The partial pressure of each gas and the corresponding amount of moles are given in table 1. In each test, after the reactor was filled with reagents, it was heated at a rate of 1 K min\(^{-1}\) to \(T_{\text{out}} = 720\) K. After heating, the reactor was cooled at a rate of \(\approx 6\) K min\(^{-1}\) to room temperature and the residual pressure of the reactants in the reactor was measured.

| Test | \(\text{H}_2\) | \(\text{O}_2\) | \(\text{N}_2\) | \([\text{H}_2]_0\) | \([\text{O}_2]_0\) | \([\text{N}_2]_0\) | \([\text{H}_2\text{O}]_0\) |
|------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1    | 1.83        | 0.90        | –           | 45.0        | 22.7        | –           | 105         |
| 2    | 1.77        | 0.80        | 4.01        | 46.4        | 21.7        | 103         | –           |
| 3    | 1.79        | 0.81        | 4.04        | 46.1        | 21.6        | 105         | 1.7         |

\(a\) Is reduced to the room temperature

### 3. Results and discussion

In each test, the molar ratio \([\text{H}_2]_0/\text{[O}_2]_0 \approx 2\). The difference from stoichiometric composition is 1% for test 1 and \(\leq 7\)% for tests 2 and 3 (table 1). The order of the \(\text{H}_2\) combustion reaction rate in the \(\text{H}_2\text{O}\) medium with respect to the hydrogen concentration is equal to 1.1, while with respect to the oxygen concentration it is less than 0.1 [12]. Consequently, the difference in initial concentrations of reagents (table 1) in tests 1 and 2 can change the combustion rate by \(\approx 3\)%, whereas in tests 2 and 3 (according to data [16]) – within 0.7%. The chemical composition of the diluent for the \(\text{H}_2/\text{O}_2\) mixture, as shown by the results of tests (figure 2), has a significantly greater effect. Figure 2 shows the results of \(T_{\text{in}}\) and \(T_{\text{in}}\) measurements depending on time, presented as a dependence \(\Delta T = T_{\text{in}} - T_{\text{out}}\) on \(T_{\text{out}}\). The estimation of the conductive, convective and radiative components of the time constant of the thermal inertia of the thermocouple junction \(\tau\) has shown that \(\tau \approx 3.3\) s. Since the maximum self-heating rate of the gas was in experiment 1 and amounted to \(dT/dt = 60\) K/min, the error of thermocouple measuring, due to the unsteady state during combustion, is \(\tau \cdot dT/dt = 3.3\) K.

With the values \(T_{\text{out}} = T_{\text{out}}^*\), which are marked with vertical arrows in figure 2, the value \(\Delta T\) begins to increase markedly due to the self-ignition of the mixture, when the heat release during the hydrogen oxidation reaction begins to prevail over the heat sink towards the reactor wall [17, 18]. The values of \(T_{\text{out}}^*\) are determined from the condition \(d\Delta T/dT_{\text{out}} - M > 3\sigma\), where \(M\) and \(\sigma\) are the expectation and standard deviation, respectively.

![Figure 2](image-url)
standard deviation $d\Delta T/dT_{ox}$ on the linear portion of the curve $\Delta T(T_{ox})$, respectively. The self-ignition temperature $T_{ix}$, shown in table 2 corresponds to the values of $T_{ox}$. This table also shows the heat capacity $C_p^*$ of the gas mixture at $T_{ix}$, calculated based on the data [1]; the oxidation duration $t_{ox}$ corresponding to the time interval from the moment of self-ignition ($T_{ix} = T_{ix}^*$) to the end of oxidation; the area $S$ under the curve $\Delta T(t)$ bounded by the baseline, and corresponding to time $t_{ox}$.

**Table 2. Experimental results.**

| Test | $T_{ix}$ (K) | $C_p^*$ (J K$^{-1}$) | $t_{ox}$ (min) | $S$ (K min) |
|------|--------------|----------------------|----------------|-------------|
| 1    | 517          | 4.3                  | 130            | 2528        |
| 2    | 514          | 3.7                  | 148            | 616         |
| 3    | 507          | 3.7                  | 145            | 540         |

According to the initial amount of reagents in tests 1–3 (table 1), the difference in the thermal effect of the hydrogen oxidation reaction will be <4%. However, figure 2 and table 2 show that the area $S$, which characterizes heat release under the curves $\Delta T(T_{ox})$ for tests 1–3, is significantly different. The reactor walls (see section 2) are covered with a layer of oxides, whereas the ferrous oxide Fe$_2$O$_3$ can have a catalytic effect on hydrogen combustion [19]. Therefore, in the conditions of this work, oxidation of H$_2$ can proceed through the mechanism of conjugate processes of heterogeneous (on the reactor wall) and homogeneous (in the volume of the reaction mixture) oxidation. Heat release in heterogeneous exothermic reactions does not affect the readings of the thermocouple $T_{ix}$ because of the high thermal conductivity (22.2 W m$^{-1}$ K$^{-1}$) and heat capacity (500 J kg$^{-1}$ K$^{-1}$) of AISI 321H steel [20] compared to the gas mixture, as well as the stabilizing effect of the thermal programming unit, which regulates the temperature of the reactor by reducing the power of the resistance heater (3, figure 1). From the initial amount of reagents in tests 1–3 (table 1), it follows that during the oxidation of H$_2$, heat in amount of ≈10.5 kJ should be released. When this amount of heat is released under adiabatic conditions, the temperature of the reactor whose mass is 3.6 kg, could only increase by ≈6 K. The essential effect of heterogeneous reactions on hydrogen oxidation is shown in [21–23].

The maximum value of $S$ was reached in test 1 (table 1). Consequently, at the oxidation of H$_2$ in the H$_2$O medium, the major portion of heat was released in the volume of the reaction mixture. This is explained by the shielding action of the reactor wall surface by the absorption layer of H$_2$O molecules [24]. At that, the chemisorption of H$_2$O results to the fact that on the surface of Fe$_2$O$_4$ the water dissociates through the reaction [25]:

$$\text{H}_2\text{O}_{ad} \rightarrow \text{OH}_{ad} + \text{H}_{ad}. \quad (1)$$

In tests 2 and 3, where nitrogen served the diluent of H$_2$O/O$_2$ mixture, a significant portion of the heat released at the reactor wall due to occurrence of heterogenic reactions. This may have occurred due to the low degree of filling of the internal surface of the reactor with molecules of N$_2$ by the moment of self-ignition. Area $S$ and temperature $T_{ix}$ in test 3 are lower than those in test 2 (table 2). One of the reasons for this is the involvement of the dissociative adsorption products of the water molecules (1), present in the insignificant amount in elementary reactions of heterogeneous oxidation of hydrogen [8].

The heat capacity of the mixture in test 1 is by 1.2 times higher than that in test 2, while the values of $T_{ix}$ are quite similar (table 2). This indicates a more intense oxidation of H$_2$ in the H$_2$O medium, which may be associated with the involvement in the oxidation reaction of the vibrationally excited O$_2^*$ molecules O$_2^* \equiv$ O$_2$(1), formed by the resonance exchange of the vibrational energy with the molecules of H$_2$O$^* \equiv$ H$_2$O(010) [26, 27]:

$$\text{H}_2\text{O}(010) + \text{O}_2(0) \leftrightarrow \text{H}_2\text{O}(000) + \text{O}_2(1). \quad (2)$$
The rate constant of translational-vibrational energy exchange $k_{TV}$, providing the transition of the molecule $\text{H}_2\text{O}(000)$ from the base state to vibrational-excited state $\text{H}_2\text{O}(010)$ at 300 K exceeds the reaction rate constant $k_{V}$ (2) by two orders of magnitude [27]. Therefore, the achievement of the equilibrium energy distribution in the gas, disturbed by reaction (2), proceeds faster than the reaction itself. At the same time, a high value of $[\text{H}_2\text{O}]/[\text{O}_2]$ in test 1 (table 1) provides a high fraction of $\text{O}_2$(1), which intensifies the oxidation of hydrogen.

Low self-ignition temperatures $T_{in}$ in tests 1–3 result from catalytic effect of oxidized reactor wall [19] and high density of reagents, contributing to the occurrence of trimolecular reactions. The evaluation of the number of pair and triple collisions, carried out according to [28], showed that in the present work, the number of triple collisions in terms of the order of magnitude is comparable to the number of pair collisions. Trimolecular collisions can increase the rate of elementary reactions of hydrogen oxidation not only by the involvement of the main reagents, but also the diluent molecules ($\text{H}_2\text{O}$ and $\text{N}_2$) due to the removal of the energy of chemical excitation. From the comparison of heat release intensity in homogeneous oxidation of $\text{H}_2$ in tests 1 and 2 (figure 2, curves 1 and 2), it follows that the triatomic $\text{H}_2\text{O}$ molecule is more effective as a third body than the diatomic $\text{N}_2$ molecule that is consistent with the data [29].

4. Conclusion
The present paper proposes the method of slow uniform heating of high-pressure stoichiometric mixtures of $\text{H}_2\text{O}$, diluted with $\text{H}_2$ and $\text{N}_2$. This method has allowed revealing features of hydrogen oxidation taking place through the mechanism of paired heterogeneous (on the reactor wall) and homogeneous (in the reactor volume) oxidation reactions. The oxidation process in the $\text{N}_2$ medium was predominantly heterogeneous, while that in $\text{H}_2\text{O}$ was homogeneous. This result is explained, in particular, by the pressure of shielding of the reactor wall with a layer of adsorbed $\text{H}_2\text{O}$ molecules. It is revealed that the $\text{H}_2\text{O}$ molecules are chemically involved in the oxidation of hydrogen on both the reactor surface and its volume. The low values of the hydrogen self-ignition temperature in these tests are explained by both the catalytic effect of the reactor wall and the high frequency of trimolecular collisions on the reactor wall and in its volume. The latter is a consequence of the high density of the initial gas mixtures components. The low self-ignition temperature in $\text{H}_2\text{O}$ medium can also be caused by vibrational pumping of $\text{O}_2$ molecules by vibrationally excited $\text{H}_2\text{O}^*$ molecules.

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