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Influence of hydrogen on the toxic substances formation process during co-incineration with natural gas

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Abstract: The hydrogen practical using problem in combustion processes at the existing boiler equipment is described. The influence of hydrogen on the combustion process is analysed, including adding moisture and its role in the toxic substances formation. The laboratory unit for experimental process at the semi-lamina front follow-up is created for research the role hydrogen in co-firing with natural gas, depending on concentrations of oxide and nitrogen dioxide in combustion products. The relations between the nitrogen oxide and dioxide concentrations in combustion products and hydrogen concentration in hydrogen peroxide solution are received. The optimal conditions for the nitrogen oxide oxidation to dioxide is identified for solutions containing hydrogen depending on the hydrogen content in them.

Keywords: hydrogen, heating system, nitrogen oxides, hydrogen peroxide, flame front.

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1. Introduction

Hydrogen has been used successfully as a raw material for many years. The main advantage of hydrogen is the high heat content per unit mass of 120.7 GJ/t, which is the main reason for using liquid hydrogen as fuel for rockets and power supply of spacecraft and aircraft, for which high energy content per unit mass is of paramount importance:

1. Soviet scientists from the Kharkiv Aviation Institute showed interest in the potential of hydrogen energy in the early second half of the twentieth century. However, due to the political situation, the results of the developments were often of a secret strategic nature and therefore could not be fully represented and discussed by the world scientific community.

2. A. Pidhornyi Institute of Mechanical Engineering Problems and the Institute of Renewable Energy of the National Academy of Sciences of Ukraine have been working on the problem for over 30 years. EU countries, the United States, Canada, Japan, and China have also been exploring the opportunities offered by hydrogen for more than 30 years.

3. There are different ways to use hydrogen - world practice shows positive results when adding 5-20% of hydrogen to natural gas (Professor Kudrya S. talks about the possibility of adding up to 25% to the gas network, transported by pipeline, the use of hydrogen technologies for the accumulation and transmission of "green" energy, production of metallurgical and chemical products, as well as the use in the transport sector).

The European initiative and strategic direction about carbon-free market and "green hydrogen" implementation stimulates the rapid development of hydrogen energy primarily as storage in the electricity market and aims to reduce to zero carbon dioxide emissions from energy, industrial facilities, and transport [1-4]. Using the hydrogen on heating installations for energy purposes includes a number of unresolved problems which due to the different characteristics of the fuel, and hence the modes of its combustion, require changes in the structural elements of furnaces, etc. Despite the problems of using hydrogen as a fuel for boilers, the developing hydrogen and hydrogen mixtures using technologies in combustion plants should be considered as a relevant.

2 Object and subject of research. Problems of hydrogen practical use in combustion processes on existing boiler equipment

Today, the use of hydrogen in heating systems of boilers and power boilers is characterized by the following problems which needs to be solved before using hydrogen both as mono-fuel and part of the fuel mixture on existing boiler equipment:

- The adiabatic hydrogen combustion temperature in air is 260^{o} higher than the adiabatic combustion temperature of natural gas;
- Low H_2 calorific value per volume unit (only 30% of the values for natural gas);
- The flame stabilization problem is not solved (separation the flame of the gas-hydrogen mixture from the nozzle) [5];
- Increasing the nitrogen oxides formation in atmosphere during the combustion hydrogen and hydrogen mixtures;
- Burning material, mainly the vortex, and its rapid destruction because of property the hydrogen to increase the metal fragility;
- The problem with the so-called “hydrogenous" atmosphere pollution exists. The hydrogen emissions negative impact as a greenhouse gas could increase significantly after reaching the planned volumes of hydrogen energy.

The difficulty lies in the obtaining permits procedure for operation, which is provided by the State Inspectorate for Industrial Safety and Labour Protection of Ukraine. According to State regulations on labor protection 0.00-5.08-96 for each boiler, that use a new fuel type, it is necessary to perform the verification calculation. Today, according to normative boiler unit’s calculation method [6] there is no such fuel as hydrogen. Such calculation can be made legitimately only after making changes and additions to this document.

3. Study purpose and objectives

1. Develop a concept, technology and laboratory unit for testing this technology, namely for the experimental study the hydrogen and natural gas mixtures combustion. Develop a methodology for necessary research.

3. Conduct the experimental research with the aim of determining the effect of changes in hydrogen content by adding hydrogen peroxide drops with different concentrations to laminar flame front of natural gas and compare with the same volume, number and technology for using distilled

water and determine the dependences that characterize the hydrogen combustion in a mixture with natural process gas and propose the recommendations for the technology of possible hydrogen mixtures in boilers combustion adaptation.

4. Target of research

At the Institute of Technical Thermophysics of the National Academy of Sciences of Ukraine is designed and manufactured an experimental stand for studying the moisture effect on the toxic substances formation during fuel combustion and described in detail in [7,8] and several experiments series conducted with it. The unit described in [8] was taken as a base, and a device for hydrogen peroxide solutions preparation and a perilstatic pump for supplying moisture to the flame front was installed.

5. Literature analysis

The hydrogen impact on the combustion process analysis is advisable to start from the well-known processes that are the parts of the hydrogen combustion overall process. Primarily, it is the moisture addition to the combustion process. The moisture acts as a heat turning into steam and decreasing the flame power. At the same time, it lowers the temperature in the combustion zone, which leads to a decrease the nitrogen oxides concentration. In addition, the water molecule disintegrates into hydrogen (H_2) and oxygen (O_2), if the energy of flame is sufficient. The released hydrogen is involved in combustion reactions, that is, in fact the process we are studying.

Moisture injection into the combustion zone is a technological method of nitrogen oxides reducing and this process is quite common [7]. Various water injection methods to the combustion zone are used: by mixing with the atmospheric airflow, by supplying sprayed water to the high-temperature zone and by using the water-fuel emulsions.

In MEI [6, fig. 4.16] for burning gas-oil emulsions at the gas-turbine units, the steam injection is used as an additive. Calculations are made for the following relative values between the fuel consumption and injected steam: $G_s / G_f = 0; 0.02; 0.053; 0.11; 0.33$ and 1.0, where Gs, Gf – weight consumption of steam and fuel respectively. With increasing the steam injection, the combustion zone is stretching in some measure and the maximum local flame temperature decreases by 80-100 K. After adding a small amount of H_2O, the CO content may decrease, and with a large amount, it may increase. The fuel NO concentration decreased by approximately 7%, which shows a weak effect of moisture additives on the fuel nitrogen oxides formation.

The moisture influence in the fuel combustion process was previously studied at the experimental stand developed by the authors [7,8]. In those studies, different volumes of distilled water drops were injected into the methane combustion zone (laminar flame). According to the conclusions, the moisture added to the combustion process with the initial products can be divided into moisture, which is involved in the chemical fuel oxidation process and which is not involved. The first one are destructed during high-temperature dissociation into H_2 and O_2 with the subsequent formation of hydroxyl OH or peroxide HO_2 radicals, which are strong oxidants and initiate the acceleration of the hydrocarbons combustion, such as CO oxidation by reaction:

$$CO+OH = CO_2 + H_2O, \tag{1}$$

$$CO+OH = CO_2 + H_2, \tag{2}$$

$$CO_2 +2H_2 = CH_4+ O_2. \tag{3}$$

Reaction (2) produces free hydrogen, which also initiates reaction chains with CO and CO_2, along with the possibility of methane recovery (CH_4) in local "cold" reduction zones by reaction (3). The second moisture, together with the one formed in the process (1) does not participate in the chemical combustion processes. It is excessive, performs only the ballast role, and removes heat from the combustion zone.

Calculation and experimental research allow determining the influence degree of the moisture content in the initial components on the hydrocarbon fuels combustion. The initial moisture in the fuel-air mixture should be about 8-9% by combustion products weight. This fact underlies the idea that the moisture content in the initial products influence the combustion process insignificantly.

Experimental data in this work were obtained for the air excess coefficient of $\alpha = 1.1$. These data illustrate that the nitrogen monoxide content increases at the beginning of the flame front and decreases behind the flame front when the combustion products temperature reduces because of the dilution and recombination reactions.

The nitrogen monoxide concentration decreases depending on the temperature and approximately repeats the changes of the last one with some delay. These results are in a good agreement with the results in [8] by the form of temperatures and concentrations of absolute values curves and also confirm the assumption, made as a result in analytical studies [9], about the mismatch between the maximum temperatures and the maximum concentrations zones.

For the most part, it is this double role of moisture that explains the variety and discrepancy of data on its effect on combustion process, resulted in various research [7-9]. There are even opposing views on this problem, from the combustion process intensification to an increase in the inefficient ballast volume. It can also be assumed that such common methods as combustion products recirculation to the flame root and flame turbulence in diffusion burners, which has the same function, provide flame root fertilization with the first type of moisture.

A decrease in temperature with a change in the excess air coefficient leads to a decrease NO concentration in the flame front both without moisture addition and with it. H2O drops addition reduces the maximum local temperature by at least 200 degrees for any excess air coefficient and the nitrogen monoxide content is also significantly decreased in this case.

Experiments showed that droplet moisture addition to the flame front provided a reduction in the maximum local temperature in the drop trace by 200 ± 10 degrees that led to decreasing the nitrogen monoxide content in the combustion products by 30-50%. Thus, the most effective NO formation reduction due to the drip moisture addition into the flame front was achieved at lower α, or at higher flame temperatures.

Authors [10] attempted to describe household burners on the possibility of their operation with a methane-hydrogen mixture in the range of $H_2 = 0 – 50\%$. The obtained results and conclusions show the possibility of applying the studied methane-hydrogen ratios on domestic gas stoves. However, these results could hardly be scaled either for industrial burners or for burners installed in existing boiler units in general, due to differences in technical characteristics.

Experimental studies expectedly showed that with increasing hydrogen content, higher temperatures are reached. However, it is impossible to estimate the effectiveness of the additional substance (ballasts) to the combustion process by calculating their thermodynamic characteristics only. It is also necessary to take into account the kinetics of the process. For example, in [7, 8] the ballasts, which are often added during staged combustion, such as excess air and steam are compared. The authors showed that with increasing maximum local temperatures of the process, the efficiency of the addition thermodynamically different ballasts converges. This can be explained by the assumption of the dominance of kinetic aspects over thermodynamic ones.

As the result of the above, we can assume that the partial uncertainty of the hydrogen impurities influence (the combustion process kinetic component) necessitates research in this direction.

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For chain radical reactions in a hydrogen-oxygen mixture at $T > 1000$ K, the branching mechanisms are relatively independent of the nature of the fuel. However, at temperatures below 1000 K, that is traditional for most boilers, they become much more complicate and depend on the fuel nature [10-14].

6. Research methods

The hydrogen effect on the nitrogen oxides formation was researched directly in the flame front at the laboratory on a stand with precision measuring instruments. The measurements scheme is shown in fig. 1.

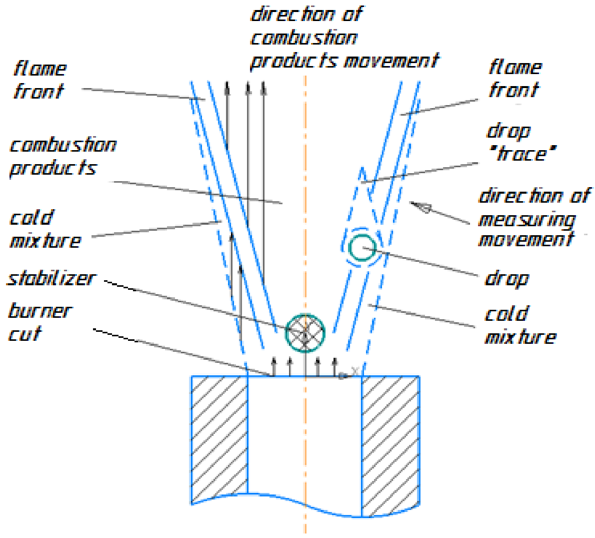

Fig 1. Measurements scheme

In experimental studies, the main attention was paid to the maximum local temperature and nitrogen oxides concentrations, which were measured in the "trace" of the drop, containing hydrogen peroxide of various concentrations from 0 to 30%. The experimental research of the normal combustion front was carried out in a stationary "reverse" flame, which is formed by continuous mixture supply to the burner after a steel cylindrical stabilizer (d = 3.0 mm). Previous research, carried out by authors, showed that within the stabilizer diameters from 1 to 5 mm, the flame front elementary structure did not depend on the one's diameter. When changed up α to 1.8, the flame front width did not exceed 2.5 mm, the mixture flow parameters corresponded to u = 1500 mm / s, Re = 250.

7. Research results

The various concentrations (up to 30%) hydrogen peroxide solution was fed in the drop of liquid form into the flame laminar methane flame front. The obtained results testified to the equidistant character of the concentrations distribution dependences during the distilled water injection.

The obtained results show the following dependence between the nitrogen oxides concentration and the hydrogen content in an aqueous hydrogen peroxide solution: with decreasing hydrogen content in the solution, and, accordantly, increasing the oxygen content, nitrogen oxides concentration increase.

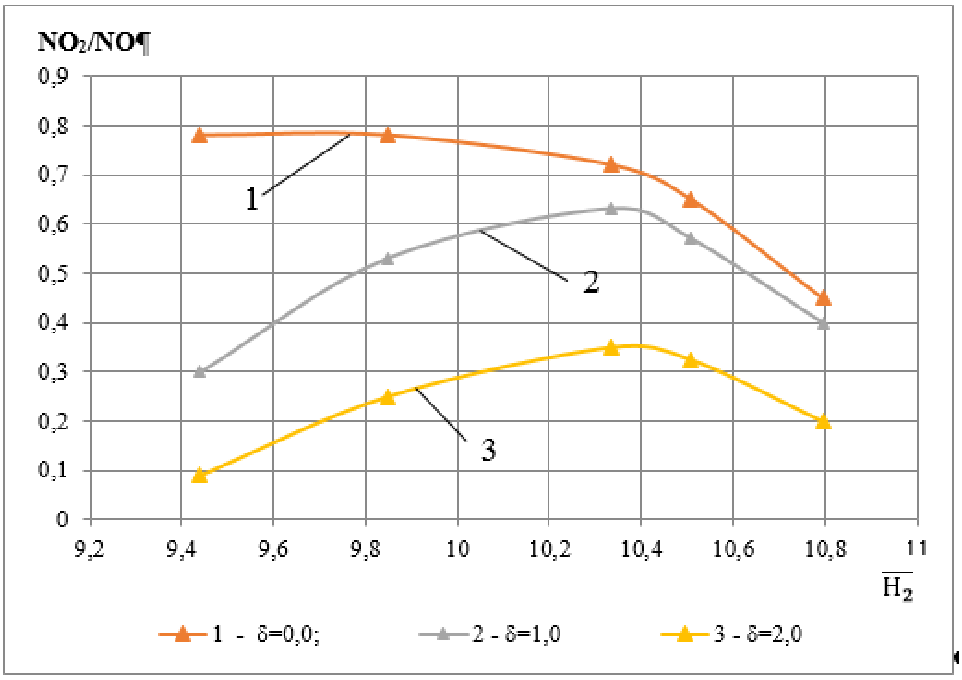

Fig. 1. The hydrogen content in the solution effect on the NO_2 formation in the laminar methane flare flame front, where:

1 - anterior front border, coordinate δ = 0,0 mm;
2 - the average front cut section, the coordinate δ = 1.0 mm;
3 - rear front boundary, coordinate δ = 2,0 mm.

In the anterior front border (Fig. 1, graph 1) the NO_2 share reaches 78% of the maximum at a 9.85% hydrogen content in solution (corresponding to concentration of H_2O_2 solution 22%), reaches the limit values and remains unchanged with further hydrogen in solution reduction that is equal to increasing in the hydrogen peroxide solution concentration. In the average front cut section (Fig. 4), graph 2 has its extremum, which corresponds to a hydrogen content of 0.63 in the ordinate. That is, a decreasing the hydrogen concentration in the solution (increasing the H_2O_2 concentration to 15%) for this cut flame front section also leads to a significant increase in the NO_2proportion. However, a further increasing the hydrogen peroxide percentage leads to a decreasing the ratio to 0.3, which roughly corresponds to the hydrogen content effect of 9.44% in the solution (3% H_2O_2 solution). Graph 3, corresponding to the point with coordinate 2.0, equidistantly repeats graph 2, but with less pronounced maximum at the point with the coordinate where the hydrogen content in the solution is about 9.4%.

Thus, temperatures above 800 ° K significantly affect the reaction rate and change the kinetics of processes. This occurs with the participation of hydrogen in a hydrogen peroxide solution. Moreover, in different front cuts, these changes are different by nature, which can be explained decreasing in the H_2O_2 existence time in the flame to 20 ms or less.

8. Prospects for further research development. The use of hydrogen and oxygen in industrial combustion processes in the near future until 2030

As a result of electrolysis of water, in addition to hydrogen, an important and high-value by-product is formed - oxygen O_2. It is much more difficult to transport to the consumer due to its explosive properties. Therefore, it is advisable to install water electrolysis units in the locations of potential oxygen consumers.

Today, oxygen is an important component of many processes in the chemical, agricultural and metallurgical industries. In energy, it has found application in the gasification of solid fuels, air enrichment for domestic and industrial boilers. It is used in incinerators , where oxygen is used.

In order to reduce emissions of pollutants and greenhouse gases in the central part of Kyiv, the authors (who are now involved in the development of the Kyiv District Heating Scheme for the period up to 2030) proposed a gradual conversion of a powerful heat source in the city center to hydrogen fuel. By 2030, it is also planned to reconstruct `Foster-Wheeler` and `CCTI` boilers, or replace them with new boilers of approximately similar capacity, with the ability to run on methane-hydrogen mixture. The decision to include the event in the promising City Development Scheme has already been discussed and approved by the customer.

During the reaction of hydrogen with carbon dioxide from the flue gases of boilers in the methanizer, synthetic methane is formed, the formed methane-hydrogen mixture (up to 10% hydrogen) is burned in an oxygen-enriched atmosphere (with electrolysis), with reduced emissions of nitrogen oxides. The carbon dioxide formed during the combustion of such a mixture is no longer considered as greenhouse gas emissions.

It is planned that electricity will be obtained from `green` energy and will be used for electrolysis of water on ST-1 until 2030 - up to 60 MW, after 2030 - until the full needs of ST-1 up to 700 MW / h. The source of water supply is the raw water of the Lybid River, with the return of clean water from the Condensation back to the river. The planned efficiency of hydrogen production reaches from 70 to 90% (energy loss of `green generation`, respectively 10-30%.). At the same time, the event allows joining the Lybid River Conservation Program, which is regulated by the Draft Law of Ukraine `On Amendments to the Law of Ukraine` On the National Targeted Program for Water Management and Environmental Rehabilitation of the Dnieper River Basin`` and the public project to save the Lybid River.

9. Conclusions

1. For the first time, on a laboratory stand with precise measuring instruments, a study was conducted with injection into the front and evaporation the coolant with variable hydrogen content [15].
2. It is shown that with increasing hydrogen content in the solution the NOx formation decreases, which can be explained by the oxygen consumption in fast reactions that require less energy.
3. It is shown that with increasing hydrogen content in the solution, the NO_2 formation increases to maximum values at $\overline{H_2} = 10{,}32\%$, and then decreases again by 70% of the maximum concentration.
4. With a decrease of the H_2 concentration in the hydrogen peroxide solution of (respectively, an increase hydrogen peroxide to 30% the concentration) H_2O ballast cooling effect in the solution decreases to zero by increasing the thermal CO oxidation effect by OH radicals, H_2O disintegration and increase the flame temperature by approximately 150°.
5. The NO_2 concentration in the relevant investigated flame front areas with the hydrogen peroxide solution injection depends on:
   a. the H_2 concentration in the solution,
   b. maximum local temperature in the flame front,
   c. points of additional ingredients injection.

The formation of up to 80% NO_2 in the composition of NOx is observed near the anterior flame front border and in the first part of the flame front that is, NO is only 20% of the NOx composition, if the hydrogen peroxide concentration is 15%.

It has been experimentally shown that the most appropriate conditions for the NO to NO_2 oxidation is the injection into the flame a solution, when the hydrogen content is 10.32% and the temperature range 800 - 1000 ° K. The flammable area rather than the flame front is suitable for these conditions. Therefore, when burning hydrogen in the boiler furnace, the NO concentration increases and the NO_2 share decreases.

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