

Cyclic Detonation of the Ternary Gas Mixture Propane–Oxygen–Steam for Producing Highly Superheated Steam

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Presented by Academician Al. Al. Berlin

Received December 5, 2019; revised December 15, 2019; accepted December 15, 2019

Abstract—Systematic experiments were performed on an innovative pulse detonation steam superheater (PDSS) for determining the concentration limits of detonation of the ternary mixtures propane–oxygen–steam at normal atmospheric pressure. The experiments were carried out while varying the fuel–oxygen equivalence ratio (from 0.3 to 1.7) and the volume fraction of steam (from 0 to 0.7). Cyclic detonation of ternary mixtures was shown to be able to create a high-temperature gas medium that has a temperature above 2250 K and contains to 80% highly superheated steam and to 20% CO₂, and also CO, O₂, and H₂ at low concentrations at atmospheric pressure. Such medium was proposed to be used for advanced treatment of household and industrial organic waste to produce a gas mixture of CO and H₂. Because the filling of PDSS with the “cold” ternary gas mixture is periodic, the increase in the temperature of its walls and internals is insignificant, and PDSS can be built from conventional (not necessarily refractory) construction materials.

Keywords: highly superheated steam, detonation steam superheater, cyclic process, gas detonation, concentration limits of detonation, organic waste recycling

DOI: 10.1134/S0012501620020025

Environmentally friendly treatment and recycling of household and industrial waste are currently one of the most urgent challenges of modern civilization. This challenge is mainly hoped to be solved by developing oxygen-free technologies based on pyrolysis, thermal decomposition, and gasification of waste in reactors in a highly superheated steam (HSS) medium at a temperature above 2000 K at near-atmospheric pressure [1, 2]. One of the proposed technological solutions is to use HSS produced by combustion of a hydrogen–oxygen mixture [1]. Another solution is to use a syngas (CO + H₂)–steam mixture preheated to the above temperature [2]. Probably, the practical implementation of such technologies would have ensured the cost-effective treatment of waste of any morphological and chemical composition with full recovery of material and energy resources contained in waste without polluting emissions. However, because

of problems of heat insulation of combustors and reactors, the above technologies have not been implemented to date even as pilot plants.

We have recently proposed [3, 4] a new method for producing HSS at a temperature above 2000 K at atmospheric pressure, in which the problem of heat insulation of the combustor and the reactor has been solved by the replacement of ordinary (deflagration) combustion by detonation combustion and steady process by cyclic process. HSS is proposed to be obtained in a pulse detonation steam superheater (PDSS) by cyclic detonation of the ternary gas mixture fuel gas–oxidizing gas–steam, with HSS forming additionally as a product of the detonation of the fuel gas. The fuel gas can be hydrogen, natural gas, propane, etc., and the oxidizing gas can be oxygen, air, oxygen-rich air, etc. The proposed [3, 4] devices allow the practical implementation of the above technologies [1, 2]: the walls and internals of PDSS are heated to a relatively low temperature (700–800 K) [5]; i.e., PDSS can be built from conventional (not necessarily refractory) construction materials.

In this work, we put forward a new method for obtaining HSS at a temperature above 2250 K at atmospheric pressure, in which the problem of heat insulation of the combustor and the reactor was solved

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by using detonation combustion instead of ordinary combustion and cyclic process instead of steady process. The studies were conducted on a specially designed test stand. The main parts of the test stand were PDSS, systems of feeding of the components of the fuel mixture and steam to PDSS, and measurement and control systems. The fuel gas was propane, and the oxidizing gas was oxygen.

The PDSS was a stainless steel circular tube 50 mm in diameter and 2.5 m in length with one open end and one closed end. The open end of PDSS was connected to a silencing chamber vented to the atmosphere. To the closed end of PDSS, propane and oxygen were fed separately and cyclically. Downstream were two ignition sources: standard car spark plugs. A 1.5-m-long Shchelkin spiral was introduced into PDSS for reliable cyclic initiation of detonation.

Propane and oxygen were fed to PDSS at a pressure of no more than 200 kPa. The source of steam fed to PDSS was a closed vessel with water and variable-power electric heaters. Steam was supplied to PDSS through a heat-insulated main steam line at an overpressure of about 10 kPa and a temperature of 375 K downstream the ignition sources. The steam flow rate was controlled by varying the power of the electrical heaters. The system of feeding of the components of the ternary mixture was adjusted so that PDSS was completely filled with the fuel mixture.

Eight ionization probes were installed along the PDSS length for measuring the detonation wave velocity according to a published procedure [6]. The error of measuring the detonation wave velocity was ± 100 m/s. The temperature of the PDSS wall was controlled with a type K (chromel–alumel) thermocouple. The temperature of steam fed to PDSS was measured by a Pt100 sensor (a platinum resistance thermometer). The average gas flow rates were determined from the pressure drop in the cylinders. The error of determining the average fuel–oxygen equivalence ratio (FOER) in the fuel mixture was 15%. The average mass flow rate of steam was found from the change in the weight of the source of steam during the experiment. The error of measuring the mass flow rate of steam was 1%. The experiment was completely controlled by an automatic control system. Initially, PDSS operated in the frequency mode without feeding steam for the tube walls to be heated to a temperature of about 378 K. Then steam was fed together with propane and oxygen to PDSS, and cycles of initiation of detonation and its propagation through the ternary mixture began to be counted. Each experiment included 20 to 40 cycles with a pulse repetition rate of 0.2 Hz. The cycle frequency was low because of the low pressures of feeding of propane and steam. In the experiments, the FOER and the volume fraction X of steam in the fuel mixture were varied from 0.3 to 1.7 and from 0 to 0.7, respectively.

As the detonation wave passes from the propane–oxygen mixture to the ternary mixture propane–oxygen–steam, three modes of propagation of the reaction front were detected: normal detonation mode, limiting mode, and decaying-detonation mode. In all the modes, the curves of detonation wave velocity versus travelled distance initially had a dip, the depth and width of which increased with increasing fraction of steam in the ternary mixture. In the normal mode, in all the operating cycles, the reaction front velocity after the dip increased and reached a plateau close to the Chapman–Jouguet thermodynamic detonation velocity [7]. In the limiting mode, a cyclic instability was observed: in some of the cycles, there was a dip in the reaction front velocity with subsequent recovery initiation of detonation and its propagation in an overdriven mode, and in the others, the front velocity progressively decreased, i.e., the detonation decayed. In the decaying-detonation mode, in each operating cycle, there was a progressive decrease in the reaction front velocity.

Figure 1 presents detonation wave velocity versus FOER at various volume fractions of steam in the ternary mixture of $X = 0, 0.3, 0.4, 0.5,$ and 0.6 .

Here and hereafter, the values of the detonation wave velocity were obtained by averaging the velocities over three measuring bases in the end part of PDSS on a segment without the Shchelkin spiral. For comparison, the curves obtained by thermodynamic calculation are shown. The measured values of the detonation velocity agree generally well with the calculation results.

Figure 2 shows the domain of the existence of cyclic detonation in the ternary mixture in the parametric plane X –FOER.

The curve separating the detonation “go” domain from the detonation “no go” domain is drawn between the experimental points corresponding to the normal detonation mode and the limiting mode (or the decaying-detonation mode). The detonation of fuel-rich mixtures with $\text{FOER} > 1$ is much less sensitive to the dilution with steam than the detonation of fuel-lean mixtures with $\text{FOER} < 1$. Whereas the detonation limit of lean mixtures with $\text{FOER} = 0.4$ – 0.8 was reached by adding 30–35% steam, the detonation limit of rich mixtures with $\text{FOER} = 1.2$ – 1.7 was attained by adding 45–50% steam. The maximum steam content (60%) at which the detonation of the ternary mixture is still possible was achieved at $\text{FOER} = 1.0$ – 1.1 . Importantly, the measured temperature of PDSS walls in the experiments did not exceed 390 K.

The good agreement between the measured and calculated values of the detonation velocity (Fig. 1) suggests that the thermodynamic calculation fits well with the experimental values of the temperature and composition of the detonation products. Figures 3 and 4 illustrate the results of the calculating the temperature (Fig. 3) and composition (Fig. 4), respectively, of

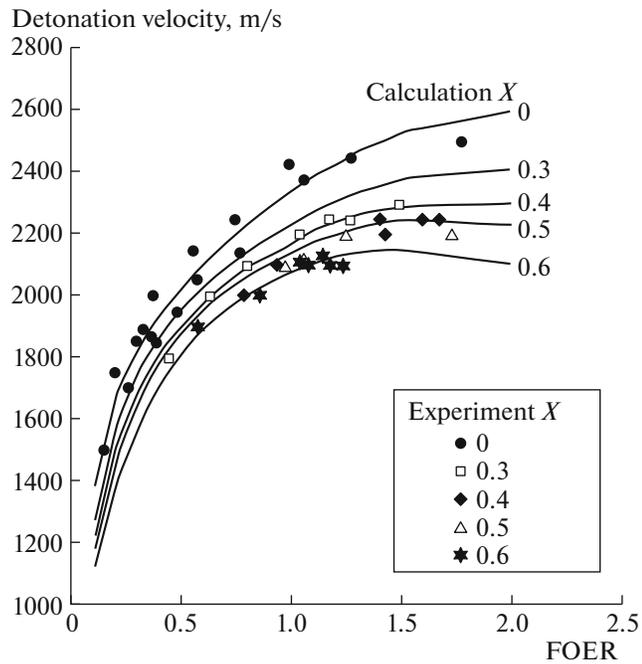


Fig. 1. Detonation wave velocity versus FOER at various volume fractions X of steam. The curves represent the results of the thermodynamic calculation; the points, the experimental data.

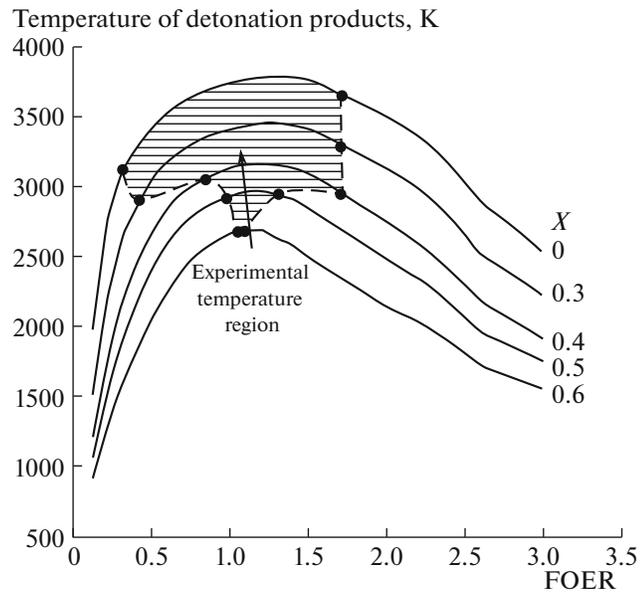


Fig. 3. Temperature of the products of the detonation of the ternary mixtures at various volume fractions X of steam (thermodynamic calculation). The shaded area shows the region in which the normal detonation mode was experimentally detected.

the products of the detonation of the studied ternary mixtures as a function of FOER and X , respectively. The shaded areas show the regions in which the nor-

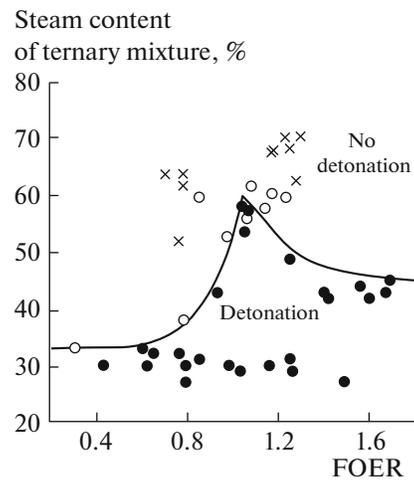


Fig. 2. Domain of the existence of cyclic detonation in the ternary mixture: (filled circles) normal detonation mode, (open circles) limiting mode, and (crosses) decaying-detonation mode.

Volume fraction in products of detonation of stoichiometric ternary mixture, abs. units

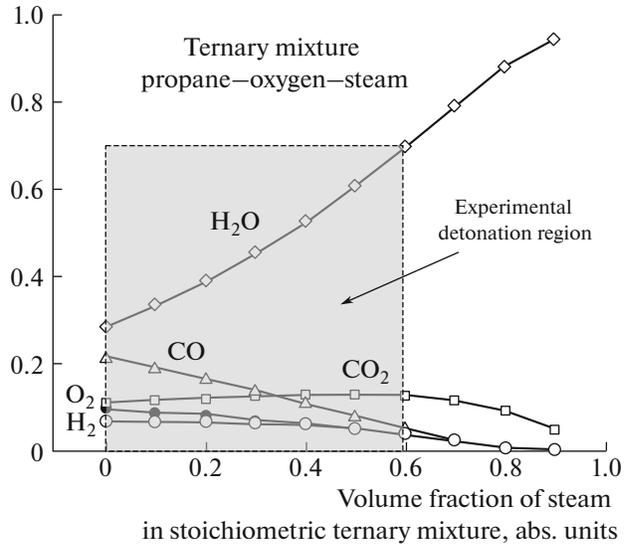


Fig. 4. Composition of the products of the detonation of the ternary mixtures at various volume fractions of steam (thermodynamic calculation). The shaded area shows the region in which the normal detonation mode was experimentally detected.

mal detonation mode was experimentally detected. One can see that the temperature of the products of the detonation of the ternary mixtures exceeds 2700 K (Fig. 3), and the maximum steam content of the products of the detonation of the stoichiometric mixture reaches 70% (at $X = 0.6$, see Fig. 4).

Along with steam, the products of detonation of such a mixture contain CO_2 (to 15%), CO (to 20%), O_2

(to 10%), and H₂ (to 7%), and in the detonation limit (at $X = 0.6$), the volumetric percentages of CO, O₂, and H₂ decrease to 5%.

According to the calculation, the pressure in the Chapman–Jouguet plane under the experimental conditions ranges from 1.3 to 3.2 MPa, i.e., significantly exceeds atmospheric pressure. As the detonation products expand to 0.1 MPa (i.e., as the detonation wave leaves PDSS and enters the atmosphere or the reactor), their temperature decreases. To determine the steam temperature after the expansion, we performed additional thermodynamic calculations. The calculations showed that the temperature of the isentropically expanded products of the detonation of the stoichiometric ternary mixture with $X = 0.6$, which consists mainly of steam (about 80%), exceeds 2250 K.

Thus, cyclic detonation of the ternary mixtures propane–oxygen–steam produces HSS with a temperature above 2250 K at atmospheric pressure, and the products of the detonation of the stoichiometric ternary mixture at the outlet section of PDSS mostly comprise HSS (to 80%) and CO₂ (to 20%), and also small amounts of CO, O₂, and H₂. It was anticipated that treatment of household and industrial organic waste by such a high-temperature medium would produce a CO–H₂ gas mixture, which can further be used both as an energy gas for PDSS and for heat and/or power generation, and as a feedstock for production of methanol and synthetic motor fuels. Because the filling of PDSS with the “cold” ternary gas mixture is periodic, the increase in the temperature of its walls and internals is insignificant, and PDSS can be built from conventional (not necessarily refractory) construction materials.

FUNDING

This work was supported by the Ministry of Education and Science of the Russian Federation (State contract no. 05.607.21.0304, contract identifier RFMEFI60719X0304) under the Federal Target Program “Research and Development in Priority Areas of Development of Science and Technology Sector for 2014–2020.”

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Translated by V. Glyanchenko