



ON THE FEATURES OF THE NEGATIVE TEMPERATURE COEFFICIENT PHENOMENON IN COMBUSTION OF N-PENTANE-AIR MIXTURES

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ABSTRACT

The ignition of n-pentane-air mixture at low temperatures is experimentally studied in a rapid mixture injection static reactor. The ignition process was monitored using a high speed color video camera. It is shown that introduction of platinum wire into the reactor eliminates the phenomenon of negative temperature coefficient; however Pt wire has no effect on the ignition delay time of thermal ignition of stoichiometric n-pentane-air mixture at lower temperatures.

Keywords: Ignition, N-pentane, Kernel, Speed filming, Negative temperature coefficient, Catalytic, Delay.

1. INTRODUCTION

Ignition or, more specifically, self-ignition of combustible systems is primarily associated with a spontaneous chemical reaction. The term “self-ignition” emphasizes the fact that the chemical reaction in the reaction medium begins and develops in the absence of external energy sources (e.g. spark discharge) under appropriate initial conditions, i.e., at a temperature, pressure, and concentration of the reagents that provide a sufficiently fast occurrence of chemical transformation.

It turns out that, despite all the variety of reacting systems and the conditions of inception and rapid development of chemical reactions in them, it is extremely difficult to determine the mechanism of ignition of the system. The problems of the theory of ignition of reacting systems were examined by such prominent scholars as N.N. Semenov, D.A. Frank Kamenetskii, S.M. Todes, Ya.B. Zel'dovich [1-4] to mention only a few. Two classes of reacting systems, which most clearly manifest the two main factors, have been identified. These are the development of a chain

reaction and heat generation, which were considered independently in the classical works on self-ignition. One of the most important features of self-ignition is the existence of limiting conditions under which the competition between transport processes (diffusion and heat transfer), removing active species and heat from the system, and chemical reactions that supply them, leads to an actual termination of the reaction. Consideration of these processes underlies the theories of chain and thermal explosions.

Studying the ignition of fuels, mainly hydrocarbons, is of obvious practical importance, but even to this day, there is no complete clarity about the mysterious phenomena accompanying this process. First of all, these are stepwise ignition and negative temperature coefficients (NTC), observed at considerably low temperatures. NTC is the increase of the delay time of ignition with temperature growth in a certain interval of temperatures. It causes undesirable phenomena in internal combustion engines [5, 6]. There is no consensus on the detailed mechanisms of hydrocarbon oxidation in this temperature range as well as on understanding of NTC phenomenon.

The ignition delay time (τ) is one of the most important macro kinetic characteristics of chain thermal ignition, which can be measured in relatively simple ways. However, all existing methods of measurement are based on different physical methods of heating the test gas, which unfortunately do not provide an instantaneous and uniform heating of the mixture to the desired temperature. In addition, they produce flows of the gas mixture and, consequently, give rise to convective mass and heat transfer and gas dynamic disturbances. This phenomenon greatly complicates the temperature distribution in the reactor. The rate of heating the mixture determines the range of ignition delay times measurable by the method used in the present work, since the time of heating the mixture determines the lower limit of the measurement range.

In addition it is known that a platinum layer on the reactor surface exhibits a promoting action on the hydrogen oxidation reaction [7] caused by heterogeneous development of reaction chains [8]. The occurrence of these heterogeneous reactions enhances the probability of spontaneous ignition of gas mixture at a surface and influences markedly on delay times of ignition. Hence, the state of the reactor surface is another factor that determines the uniformity of ignition.

Really, according to [9, 10] in the shock tube and rapid compression machine, self-ignition is of kernel nature. We have recently shown [11] that the ignition of the n-pentane-air mixtures in a rapid mixture injection static reactor at atmospheric pressure begins with the appearance of an initial center at the most chemically active site of the surface. The center initiates the propagation of hemispherical flame front with the normal velocity corresponding to the temperature of the reactor walls and gas mixture composition; *i.e.* thermal ignition includes the stages of warming up, local ignition and flame propagation. Therefore, the combustion process begins with kernel ignition by the heated chemically active surface. Therefore the reaction never starts in the entire

volume. In all likelihood, kernel ignition is a rule rather than exception. Homogeneous ignition (once at all points of the volume) is an ideal case, which has not yet been observed experimentally [12, 13].

The work is aimed at establishment of the influence of catalytic surface (Pt wire) on the existence of the negative temperature coefficient phenomenon in combustion of n-pentane in air.

2. EXPERIMENTAL

The ignition of n-pentane-air mixtures was studied in a rapid mixture injection static reactor (Fig. 1). According to this method, a premixed fuel-air mixture passes from a storage vessel through a solenoid valve into a reactor, preliminary evacuated and heated to the desired temperature. The stainless steel reactor, 12 cm in inner diameter and 25 cm in length, consisted of hemispherical and cylindrical parts and was equipped with the window made of KU-1 quartz. The diameter of the viewing part of the window was 11 cm, making it possible to fully visualize the process in the reactor. The design of the heater provided a uniform temperature distribution in the reactor volume, which was controlled with a movable thermocouple placed at the reactor surface.

Experiments were carried out with stoichiometric n-pentane-air mixtures over the pressure range of 2-3 atm. The light emission that accompanied the ignition was recorded with a Casio Exilim F1 Pro color digital video camera (operating at a frame speed of 300 to 1200 frames/s), sensitive over the spectral range of 420-740 nm, connected to a computer. The pressure time history was recorded with a Karat-CI piezoelectric transducer, the signal from which was fed through an ADC into the computer. Before each experiment, the reactor was evacuated with a 2NVR 5D backing pump. The pressure in the reactor was measured by a standard vacuum gauge. An electromagnetic valve was used to open and close gas lines. At the moment of the valve opening, a light-emitting diode was turned on; its flash was recorded by the camera. It allowed us determining the delay time of thermal ignition from a shot sequence for each separate ignition with high accuracy. N-pentane "Merck" of chemically pure grade was used.

3. RESULTS AND DISCUSSION

By means of the direct measurements [14] of temperature at the center of the reactor (10 cm in diameter and 10 cm in length) with thin 25 mm thermocouples at atmospheric pressure and 800-980 K it was shown that the time of warming up of gas mixture does not exceed 0.2 s. It is much less than the time obtained with the formula considering only conductive heat exchange. It means that the error of $\square\square$ measurement is of the same order of magnitude.

We performed the following experiments to determine whether the reactor surface produces a catalytic effect on the ignition of hydrocarbons. To do this, we introduced into the reactor a platinum wire 0.5 mm in diameter and 0.5 m in length. Figure 2 displays a photograph showing

the location of the wire in the reactor (the left frame), as well as frames showing the first moments of ignition of the pentane–air mixture in the presence of the catalytic surface. As can be seen from these filming frames (Fig. 2, shots 1-4), ignition kernels occur along the wire.

Figure 3 compares the ignition delay times for a stoichiometric pentane–air mixture in this reactor in the presence and absence of the catalytic surface. As is evident from the experiments, in the region of positive temperature coefficient, the catalytic surface produces almost no effect on the ignition delay time, i.e. on the process of ignition. However, in the region of negative temperature coefficient, the role of the catalytic surface becomes very significant. The ignition delay time continues to decrease with increasing temperature, rather than increase, as is commonly observed in the NTC region. The high speed filming frames shown in Fig. 2 correspond to the beginning of the NTC region. Figs 4 and 5 display pressure oscillograms for ignition under the same conditions in the absence and the presence of the catalytic surface, respectively. Figure 5 shows the staging in the process of ignition in the presence of a catalytic surface in the reactor, whereas the oscillogram in Fig. 4 shows that, in the absence of the catalyst, cool flame ignition accompanied with considerably smaller warming up (if any arises at all) immediately transforms into hot one.

Experimental data show that the mechanism of ignition under real nonideal conditions is much more complex than that considered in classical theories. Unfortunately, the fact of existence of ignition kernels does not shed light on the mechanism of low temperature phenomena, such as negative temperature coefficient, stepwise ignition, and cool flames. Visually observed ignition kernels develop very rapidly, signifying in fact the beginning of hot ignition, while stepwise ignition and cool flames precede the stage of hot ignition. Although the pressure time history of the process is indicative of a cool flame ignition of the mixture, which manifests itself as a small step that precedes the main rise in pressure and appears much earlier than the ignition kernel recorded by the camera, filming frames show no detectable cool flames. Apparently, cool flames cannot be observed in visible light, since the temperature rise in these cases is not high enough for the appearance of luminous intermediate products, whereas the brightness of the light emission is not sufficient to be recorded by a high speed video camera.

A peculiar effect on the ignition is produced by the introduction into the reactor of a catalytic surface in the form of a platinum wire (Fig. 2). It turned out that, in different temperature regions, this catalytic surface influences the ignition differently. At low temperature, the catalytic surface has no appreciable effect on the ignition delay time. However, in the temperature region in which NTC is usually observed, the presence of the same surface eliminates this phenomenon. In this case, the centers of catalyzed ignition are located along the surface of the wire, i.e., it serves as an ignition source. Since the ignition delay in this case behaves as if there is no difference between cool flame and hot ignition in the temperature region corresponding to NTC, we can conclude that the catalytic surface eliminates a certain stage of inhibition after the emergence of the cool

flame. In our opinion, this fact is very important for further studies and for elucidating the nature of the intermediate products of the reaction causing the existence of NTC phenomenon. Therefore it is of interest to apply both other forms of the catalyst Pt (other than wire, the first effort is presented in [13]), and different sets of experimental conditions especially based on application of chemically active additives to allocate elementary reactions responsible for the phenomenon.

The aforementioned phenomena raise the question of the kinetic information value of measurements of the ignition delay time, which constitute the basis for modeling combustion processes in various conditions, including deflagration to detonation transition. Unfortunately, there is no direct answer to this question, because it would require measuring the characteristics of both temperature fluctuations in the entire volume occupied by the mixture (their size and lifetime) and the distribution of active sites on the reactor surface, which is instrumentally unfeasible to date.

4. CONCLUSIONS

It is experimentally shown using rapid mixture injection static reactor that at temperatures < 660K, the catalytic Pt surface has no appreciable effect on the ignition delay time of thermal ignition of stoichiometric n-pentane-air mixture. However, in the temperature region in which negative temperature coefficient is usually observed, the presence of Pt surface eliminates NTC occurrence. The revealed feature seems to be the key one for understanding NTC phenomenon.

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Figures

Fig-1. Schematic diagram of the experimental setup:(1) reactor, (2) electric heater, (3) thermal insulation, (4) valves, (5) mixer, (6) digital video camera, (7) optical window, (8) semispherical inset, (9) pressure transducer, (10) ADC-computer based data acquisition system, (11) digital voltmeter, and (12) spark ignition circuit.

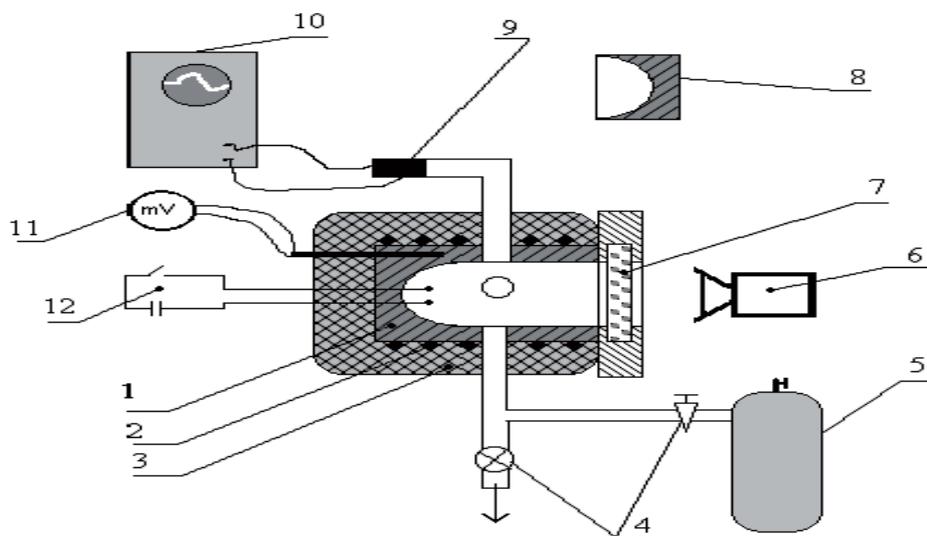


Fig-2. The left frame: location of the platinum wire in the reactor; (1–4) consecutive frames of ignition of pentane–air stoichiometric mixture recorded at a frame speed of 600 frames/s. Initial conditions: a pentane–air stoichiometric mixture, $T_0 = 638$ K, $P_0 = 2$ atm.

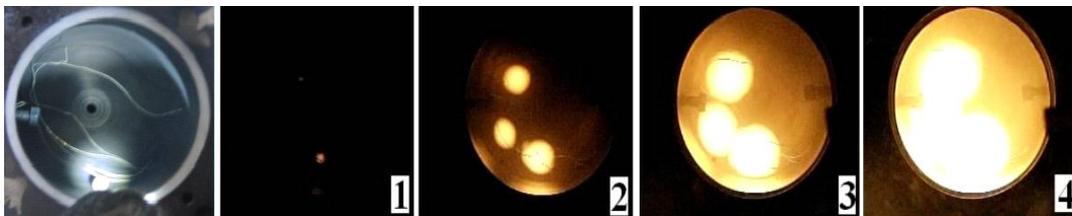


Fig-3. Temperature dependence of the ignition delay time τ for pentane–air stoichiometric mixture at an initial pressure of 3 atm. The squares and triangle represent the ignition delay times in the absence and presence of a catalytic surface, respectively.

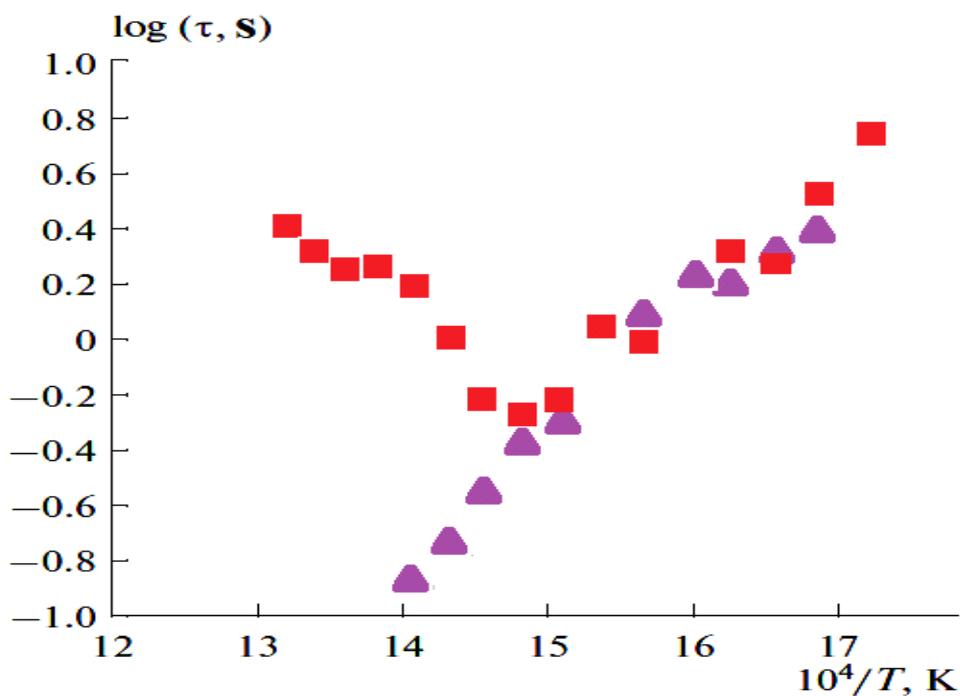


Fig-4. Typical oscillogram of the change in pressure for the ignition of a pentane–air stoichiometric mixture near the NTC region in the absence of the catalytic surface at initial pressure and temperature of 2.9 bar and 687 K; $\tau = 0.585$ s.

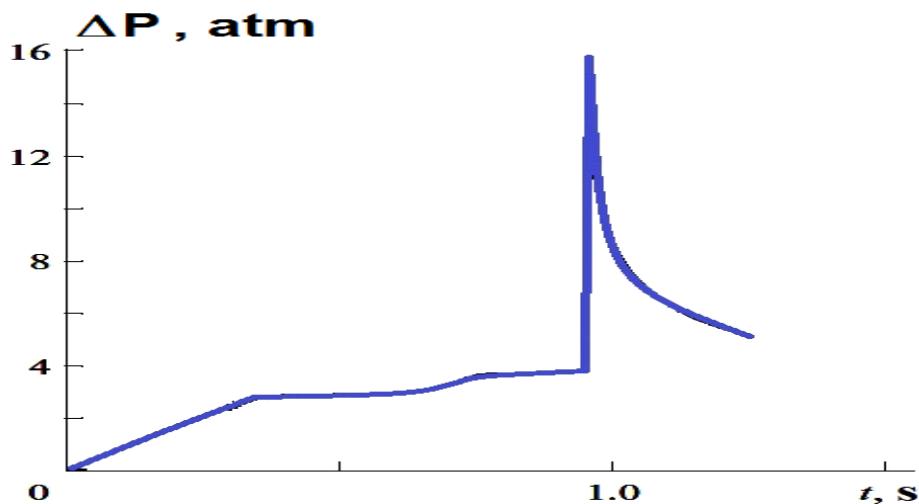
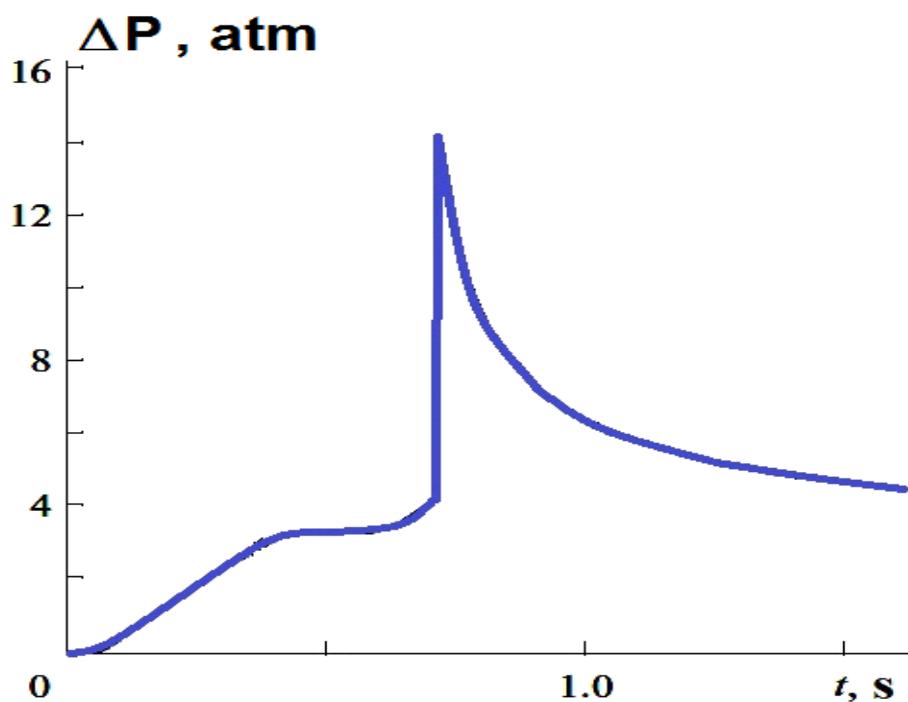


Fig-5. Typical oscillogram of the change in pressure for the ignition of a pentane–air stoichiometric mixture near the NTC region in the presence of the catalytic surface at initial pressure and temperature of 2.9 bar and 687 K; $\tau = 0.275$ s.



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