

# IGNITION IN ETHANOL-CONTAINING MIXTURES AFTER HIGH-VOLTAGE NANOSECOND DISCHARGE

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## ABSTRACT

We study the kinetics of ignition in lean and stoichiometric  $C_2H_5OH:O_2:Ar$  mixtures after a high-voltage nanosecond discharge. Ignition delay time above the self-ignition threshold is measured in a shock tube with a discharge cell. Creation of the discharge plasma is shown to lead to a significant decrease in ignition delay. Discharge processes followed by chain chemical reactions with energy release are simulated during ignition in the  $C_2H_5OH:O_2:Ar$  mixtures. Good agreement is obtained between calculated and measured ignition delay times. It is shown that the effect of the discharge plasma on ignition of the ethanol-containing mixtures is associated with active species production in the discharge phase. A method is suggested to compare the effect of nonequilibrium pulse discharge plasma on ignition in different fuel-air and fuel-oxygen mixtures above self-ignition temperatures. It is shown that, in all mixtures under consideration, this effect is more profound at lower gas temperatures and for fuels with low reactivity.

## 1. INTRODUCTION

Ethanol oxidation recently attracted considerable attention of researchers due to its application as a neat fuel, octane enhancer, fuel extender, and oxygenate. Using ethanol in transportation fuels, it is possible to meet octane quality demands and reduce undesirable emissions simultaneously. Applications of oxygenated fuel like ethanol is expected to increase as regulations on pollutant emissions become stricter. In addition, ethanol possesses the advantage of being produced from renewable fuels like biomass.

In recent years, considerable interest has been drawn to applications of non-equilibrium plasma for plasma-assisted ignition (PAI) and plasma-assisted combustion (PAC) [1, 2]. It was shown experimentally and numerically that nanosecond discharge plasmas have profound effect on ignition delay reduction and flame stabilization in various combustible mixtures. As a result, ignition by non-equilibrium gas discharges seems to be perspective for a number of applications under conditions of high speed flows and under conditions similar to automotive engines.

Most studies of PAI and PAC have dealt with  $H_2$ , alkanes from  $CH_4$  to  $C_5H_{12}$ , ethylene and acetylene. The purpose of this paper was to study the ignition of  $C_2H_5OH:O_2:Ar$  mixtures behind a shock wave under the action of a high-voltage nanosecond discharge producing a quasi-uniform nonequilibrium plasma. To clarify the effect of discharge plasma on ethanol ignition, measurements were also made in the absence of the discharge. A kinetic mechanism of the effect of nonequilibrium plasma was studied by simulating numerically the discharge and ignition characteristics and comparing calculated results with measurements. Observations of ethanol ignition were compared with data on ignition of other fuels.

## 2. EXPERIMENT

A detailed description of the experimental setup and methods used to study plasma-assisted ignition has been given elsewhere [3, 4]. We used the shock tube ( $25 \times 25$ -mm<sup>2</sup> square cross section) with a 1.6 m long working channel and a 60 cm long high – pressure cell. The stainless – steel working channel had two pairs of windows

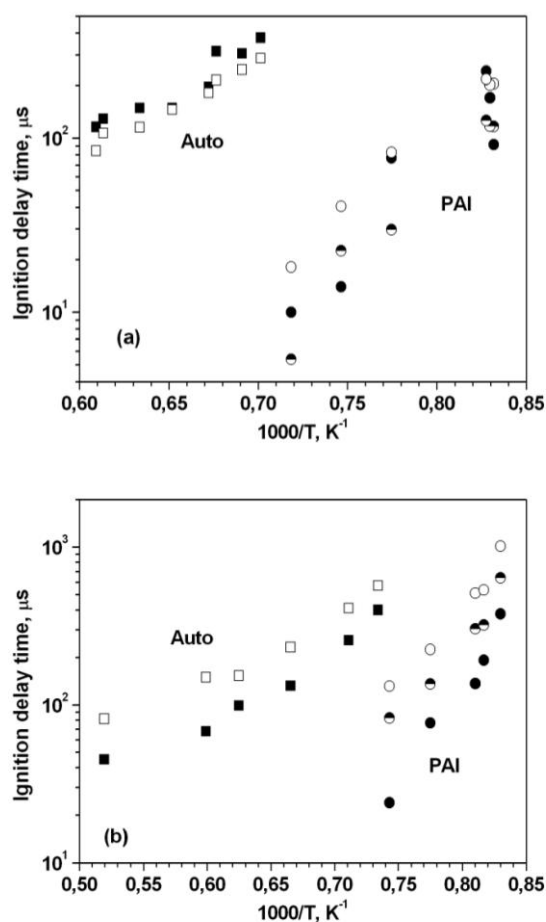
for optical diagnostics along its length. There were eight optical windows in the last plexiglas discharge section of the shock tube. The metal end plate of the tube was a high – voltage electrode, whereas the grounded steel section of the shock tube was used as another electrode. A high-voltage nanosecond discharge was initiated at the instant when the reflected shock wave arrived at the observation point. The discharge developed as an ionization wave producing a quasi-uniform nonequilibrium plasma with a high density of active species.

We investigated ignition in stoichiometric ( $\phi = 1$ ) and lean ( $\phi = 0.5$ )  $C_2H_5OH:O_2$  mixtures (10%) diluted with Ar (90%). The gas temperature behind the reflected shock wave ranged from 1200 to 1500 K and the corresponding pressure ranged from 0.38 to 0.70 atm. The gas pressure and temperature behind the reflected shock wave were obtained when analyzing the data on measured velocity of the shock wave. Ignition delay time was determined from the onset of the leading front of the CH emission at 431 nm. Two capacitive gauges and a magnetic current gauge allowed us to measure the time evolution of the voltage drop along the cell and discharge current. These data were used to determine the evolution in time of the reduced electric field  $E/N$  ( $N$  is the gas number density) and energy input. The specific deposited energy increased with gas temperature and was in the range 0.04-0.09 eV/mol.

Figure 1 shows the measured delay times for autoignition and plasma-assisted ignition in lean and stoichiometric  $C_2H_5OH:O_2:Ar$  mixtures. Additional nonequilibrium excitation leads to a strong (around an order of magnitude) decrease in the ignition delay time. The effect is more profound for higher gas temperatures at which the specific deposited energy is higher.

### 3. CALCULATED RESULTS AND COMPARISON WITH MEASUREMENTS

Under the conditions studied, the discharge processes occurred on a nanosecond scale, whereas ignition developed at times longer than tens microseconds. In this case, the effect of the discharge plasma is primarily reduced to the accumulation of active species that influences the following ignition processes. In this work, the evolution in time of the density of active



*Fig. 1. The measured (closed symbols) and calculated (open symbols) delay time for autoignition and plasma-assisted ignition (PAI) in (a) lean and (b) stoichiometric  $C_2H_5OH:O_2:Ar$  mixtures as a function of the gas temperature behind a shock wave. Semiclosed symbols correspond to calculations taking into account fast gas heating during the discharge and its afterglow.*

particles was calculated in the discharge phase and in the discharge afterglow based on a numerical solution of the corresponding balance equations. The zero-dimensional approximation was used because optical observations [4] and the analysis of the discharge current waveforms showed that the discharge is uniform in our case. Active particles under consideration were excited Ar atoms and  $O_2$  molecules, O and H atoms, hydrocarbon radicals, electrons and positive ions.

We considered electron-impact dissociation, excitation and ionization of molecules and atoms, quenching of electronically excited particles, charge exchange in collisions between ions and neutral particles and dissociative electron-ion recombination, the dominant mechanism of electron loss in the discharge afterglow in our case. The rate constants for processes between ions and neutral particles were taken from the literature. The rate

coefficients for electron impact processes were calculated by solving the electron Boltzmann equation in the classical two-term approximation.

In our calculation, the production and loss of active particles was simulated in the discharge and in its afterglow. In the discharge, active particles were produced due to electron collisions with neutral particles. In the discharge afterglow with zero electric field, charged particles were removed due to dissociative electron – ion recombination to generate additional amount of atoms and radicals. These particles were also produced due to charge exchange of positive ions in collisions with hydrocarbon molecules and due to quenching of excited Ar atoms by oxygen and hydrocarbon molecules. Calculations based on a numerical solution of the Boltzmann equation for electrons showed that, under the conditions studied, most of electron energy is spent on dissociation of molecules and excitation of Ar atoms. As a result, dominant active species were atoms and hydrocarbon radicals produced (i) directly due to electron-impact dissociation of  $O_2$  and  $C_2H_5OH$  molecules and (ii) indirectly due to electron-impact excitation of Ar atoms followed by the quenching of the excited states with molecule dissociation. The densities of atoms and radicals left in the late afterglow were used further as input parameters to simulate ignition in the mixtures.

Figure 2 shows the temporal evolution of mole fractions for active species generated in the discharge. The dominant active species were O and H atoms and  $C_2H_4OH$  radicals, whereas the density of charged particles was much lower.

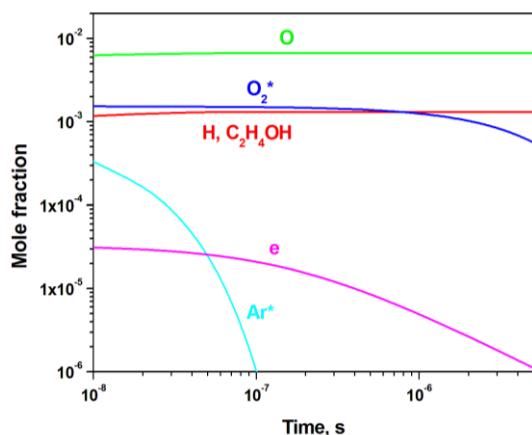


Fig. 2. The evolution in time of mole fractions for different active species in the discharge afterglow in the stoichiometric  $C_2H_5OH:O_2:Ar$  mixture at 0.45 atm and 1350 K.

The mole fraction of electrons was around  $10^{-5}$  in the discharge phase and decreased rapidly in its afterglow. Therefore, the contribution of electron-ion recombination and ion-molecule reactions into neutral species chemistry was small, as compared with electron-impact dissociation and dissociation in quenching collisions with excited neutral particles.

A zero-dimensional simulation of ignition under the action of the discharge was performed at constant pressure. Ignition phase in the  $C_2H_5OH$ -containing mixtures was modeled using the kinetic scheme [5]. We calculated ignition delay time from the analysis of the temporal evolution of CH mole fraction in the ignition phase. Delay times calculated in this work for autoignition and plasma-assisted ignition are compared in figure 1 with the measured data.

There is good agreement between the calculations and measurements for autoignition. Agreement for ignition after the discharge is not so well. The difference between calculated and measured values of ignition delay time could be associated with the effect of fast gas heating in the discharge and in its afterglow. To estimate this effect, we also made calculations assuming that 30% of the energy spent on excitation of electronic states, dissociation and ionization is quickly transferred into heat. Figure 1 shows that this effect can be important at high gas temperatures when the specific deposited energy is sufficiently high.

It is interesting to compare the effect of nonequilibrium discharge plasma on ignition for different fuels. For this purpose, we analyzed the results of this work and the results of previous shock-tube studies of this effect in various hydrogen- and hydrocarbon-containing mixtures and at various values of the specific deposited discharge energy,  $\epsilon$  [2]. The results were recalculated to reduce the ratio  $\tau_{auto}/\tau_{PAI}$  to  $\epsilon = 0.1$  eV/molecule under the assumption that  $\tau_{auto}/\tau_{PAI} = \exp(\epsilon/\epsilon_0)$ ; this formula approximated well the available experimental data. Here,  $\tau_{auto}$  is the autoignition delay time,  $\tau_{PAI}$  is the ignition delay time for PAI and  $\epsilon_0$  is the characteristic specific deposited energy for a given combustible mixture. The values of  $\epsilon_0$  were calculated using the measured values of  $\tau_{auto}$ ,  $\tau_{PAI}$  and  $\epsilon$ .

Figure 3 compares the obtained values of the ratio  $\tau_{auto}/\tau_{PAI}$  for different fuels. As would be

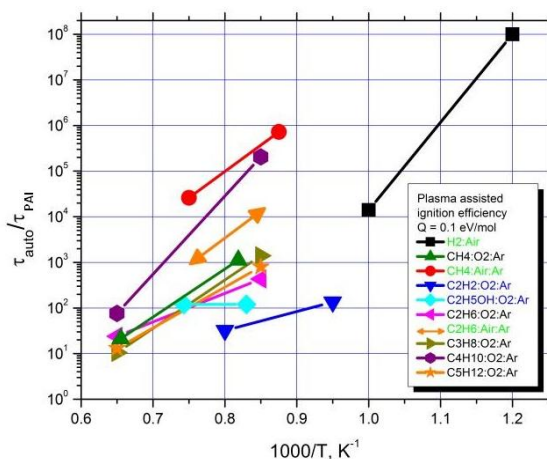


Fig.3. The ratio between the autoignition delay time and delay time after a pulsed nanosecond discharge occurring at a specific deposited energy of 0.1 eV/mol.

expected, the effect is much more profound for lower gas temperatures when the rate of thermal production of radicals is low.

Among the fuels studied, the effect of nonequilibrium plasma is smaller for acetylene and ethanol, the fuels that are easily ignited even without plasma excitation. In this case, additional generation of radicals in discharge plasma competes with thermal dissociation of molecules, the process that is efficient in acetylene- and ethanol-containing mixtures. In contrast to this, the effect of nonequilibrium plasma is profound for ignition in hydrogen- and methane-containing mixtures in which thermal dissociation is small even at relatively high gas temperatures and, at a given stoichiometric ratio, fuel fraction in a mixture is high.

#### 4. CONCLUSIONS

We have made an experimental and numerical study of the ignition in lean and stoichiometric  $\text{C}_2\text{H}_5\text{OH}$ -containing mixtures under the action of a high-voltage nanosecond discharge and showed that its initiation leads to a noticeable decrease in ignition delay time. The calculated

results agree reasonably with measured ignition delay times. Under the conditions considered, the main mechanism of the effect of gas discharge on the ignition of ethanol is the electron-impact dissociation of  $\text{O}_2$  and  $\text{C}_2\text{H}_5\text{OH}$  molecules in the discharge phase; this leads to an essential increase in the density of O and H atoms and hydrocarbon radicals at the beginning of ignition.

A method was suggested to compare the efficiency of nonequilibrium plasma ignition for different combustible mixtures after a pulse discharge at gas temperatures above self-ignition threshold. It was shown that, for all mixtures studied, the effect of nonequilibrium plasma on ignition becomes more profound with decreasing gas temperature and decreasing rate of thermal production of radicals. The relative change in the ignition delay time due to gas excitation by discharge plasma is higher for fuels (i) with low reactivity ( $\text{H}_2$  and  $\text{CH}_4$ ), (ii) with low rate of thermal dissociation and (iii) with high fraction in combustible mixtures.

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