Plasma-assisted ignition and deflagration-to-detonation transition

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Non-equilibrium plasma demonstrates great potential to control ultra-lean, ultra-fast, low-temperature flames and to become an extremely promising technology for a wide range of applications, including aviation gas turbine engines, piston engines, RAMjets, SCRAMjets and detonation initiation for pulsed detonation engines. The analysis of discharge processes shows that the discharge energy can be deposited into the desired internal degrees of freedom of molecules when varying the reduced electric field, $E/n$, at which the discharge is maintained. The amount of deposited energy is controlled by other discharge and gas parameters, including electric pulse duration, discharge current, gas number density, gas temperature, etc. As a rule, the dominant mechanism of the effect of non-equilibrium plasma on ignition and combustion is associated with the generation of active particles in the discharge plasma. For plasma-assisted ignition and combustion in mixtures containing air, the most promising active species are O atoms and, to a smaller extent, some other neutral atoms and radicals. These active particles are efficiently produced in high-voltage, nanosecond, pulse discharges owing to electron-impact dissociation of molecules and electron-impact excitation of N2 electronic states, followed by collisional quenching of these states to dissociate the molecules. Mechanisms of deflagration-to-detonation transition (DDT) initiation by non-equilibrium plasma were analysed. For longitudinal discharges with a high power density in a plasma channel, two fast DDT mechanisms have been observed. When initiated by a spark or a transient discharge, the mixture ignited simultaneously over the volume of the discharge channel, producing a shock wave with a Mach number greater than 2 and a flame. A gradient mechanism of DDT similar to that proposed by Zeldovich has been observed experimentally under streamer initiation.

Keywords: plasma; combustion; detonation; nanosecond discharge; electric field; excitation

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1. Introduction

The application of thermally equilibrium plasma for combustion control dates back more than 100 years to internal combustion engines and spark ignition systems. The same principles still demonstrate high efficiency in different applications. Recently, particular interest has been developed in non-equilibrium plasma for ignition and combustion control [1,2]. The reason for the interest lies in new possibilities for ignition and flame stabilization, which are proposed for the plasma-assisted approach. During the past decade, significant progress has been made in understanding the mechanisms of plasma-chemistry interactions, energy redistribution and the non-equilibrium initiation of combustion. A wide range of different fuels has been examined using different types of discharges [3].

There are several mechanisms that affect a gas when using a discharge to initiate combustion or stabilize the flame. There are two thermal mechanisms: (i) gas heating owing to energy release leads to acceleration of the chemical reactions and (ii) inhomogeneous gas heating generates flow perturbations, which provoke turbulence and mixing. Non-thermal mechanisms include the following: (i) the ionic wind effect (momentum transfer from an electric field to the gas owing to space charge), (ii) ion and electron drift, which, in the electric field, can lead to additional fluxes of active radicals in the gradient flows, and (iii) the excitation, dissociation and ionization of the gas by electron impact, which leads to non-equilibrium radical production and changes the kinetic mechanisms of ignition and combustion. These mechanisms, either together or separately, can provide additional combustion control, which is necessary for ultra-lean flames, high-speed flows, cold low-pressure conditions of high-altitude gas turbine engine (GTE) relight, detonation initiation in pulsed detonation engines (PDEs) and distributed ignition control in homogeneous charge compression ignition (HCCI) engines, among others.

Extensive efforts have been applied to circumvent several challenging engineering problems associated with the development of PDEs. These include fuel injection and mixing, repetitive detonation initiation, integration of detonation tubes with inlets and nozzles, and overall system optimization [4,5].

The propulsive performance of air-breathing PDEs has been theoretically and numerically studied over a wide range of system configurations, operating parameters and flight conditions. Many of the analytical papers and articles detailing the thermodynamic advantages of detonation-based combustion often assume that a detonation, for practical hydrocarbon fuels, is readily achieved. For example, in [6], a performance map was established over a flight Mach number range of 1.2–3.5. It was shown that the PDE outperformed its RAMjet counterpart for all the flight conditions considered, while the net benefit decreased with increasing flight Mach number and approximated that of the RAMjet at a Mach number of approximately 5.

The application of detonation-based combustion has been proposed for a very wide range of technical applications, from basic, ‘pure’ PDE systems for high-speed propulsion to hybrid gas-turbine systems [4,7–9]. PDE systems rely on the continued development and demonstration of technologies that produce reliable ignition and effective detonation initiation in practical hydrocarbon mixtures [10–12]. Most efforts in the past have utilized either high-energy initiators [9,10],
Starikovskiy et al. Shchelkin spirals, or obstacles with substantial blockage ratios [4,13] to initiate a deflagration-to-detonation transition (DDT). The use of high-energy initiators to initiate DDT in fuel–air mixtures is impossible for systems operating over thousands of cycles [14]. ‘Pre-detonation’ in a smaller combustor and detonation transmission into a main detonation chamber has been analysed by others [15,16], but this approach seems to be impractical because of complexity. The most common and popular approach to initiate DDT in the PDE combustor is using a Shchelkin-like wall spiral [17–19] and wall turbulence devices and their variants. Unfortunately, the conventional gas-dynamic methods of flame acceleration lead to an efficiency decrease in the detonation cycle; gas-dynamic actuators exposed to very high thermal fluxes have an extremely short lifetime, and there is no possibility of flexible control of the DDT process.

As an alternative to gas-dynamic initiation of DDT, Starikovskiy [20] proposed using a distributed, non-equilibrium gas-discharge plasma for preliminary gas excitation and reduction of the chemical induction time in the mixture. It was shown that synchronization of the ignition of different parts of the gas using gas-discharge excitation could lead to a sufficient reduction in the DDT length and time. In general, two different geometries of the discharge are possible, i.e. with radial and longitudinal plasma filament formation.

An experimental demonstration of a longitudinal, high-voltage, nanosecond gas-discharge application for detonation initiation (in a smooth-wall tube) has been performed [21]. Three modes of flamefront propagation, deflagration, transient detonation and Chapman–Jouguet (CJ) detonation, were observed. Simultaneously, experiments were carried out to determine the effectiveness of a transient plasma to initiate detonation in a short tube with radial propagation of the streamers [22]. A high-voltage pulse produced a plasma discharge consisting of many radial streamers. The transient plasma initiated low-speed combustion, a deflagration, which can undergo transition to detonation.

To analyse the possibilities of plasma-stimulated detonation in this paper, we will consider the fundamental mechanisms of plasma-assisted combustion and present recent results on detonation initiation by non-equilibrium, distributed plasma in different geometries. The first part of the paper includes a general description of different gas discharges and a brief analysis of electron energy distribution in plasma. Then, different types of gas excitation (rotational, vibrational, electronic), dissociation and ionization are analysed from the point of view of ignition initiation efficiency. Applications of plasma-assisted ignition for deflagration initiation and DDT are discussed for two different discharge geometries: transverse and longitudinal ionization wave propagation.

2. Physics of plasma-assisted ignition

A review of recent experimental studies of non-equilibrium plasma-assisted ignition and combustion can be found in the literature [1,2,23]. Over past years, considerable progress has been made in understanding the mechanisms of plasma-assisted combustion in various mixtures, including mixtures containing hydrocarbons [3]. The mechanisms were validated by making experiments under controlled conditions and by comparing the results with numerical simulation of the discharge and combustion processes. In this work, the methods of generation
of chemically active discharge plasma and the mechanisms of ignition and combustion control by non-equilibrium plasma are discussed. The difficulties of these studies and some unsolved problems are discussed. The number of works devoted to plasma-assisted combustion is exceedingly large. Therefore, this survey does not cite all the available literature. Instead, we have attempted to present only new results and to show the main obstacles for further progress in the use of non-equilibrium plasma in favouring combustion processes.

(a) Discharge energy branching

The major difference between common combustion and plasma-assisted combustion is an extreme non-equilibrium excitation of the gas in the discharge. An external electric field accelerates electrons. Energy exchange between electrons and the translational degrees of freedom of molecules is very slow because of large differences in mass. This means that electron impact can transfer the energy to the internal degrees of freedom of the molecules only. If the rate of internal energy relaxation is not very high, the population of the excited states of the molecules will be very far from the initial Boltzmann energy distribution. Overpopulation of excited states, dissociation and ionization of the molecules, which could be followed by ultraviolet generation and additional gas heating, leads to an increase in the system reactivity and facilitates ignition and flame propagation. From this point of view, the most important question for plasma-stimulated chemistry is the discharge energy branching through different degrees of freedom of the molecules, the rate of system relaxation (thermalization) and the chemically active system response to this non-equilibrium excitation.

The rate of the excited level population in the discharge depends on the electron energy. The lowest energy is needed for excitation of the rotational degrees of freedom. A typical rotational quantum is of the order of few Kelvin, and the electron energy at approximately 300 K (approx. 0.03 eV, where 1 eV \( \sim 1.602 \times 10^{-19} \) J) is enough for efficient excitation of molecular rotations. A typical quantum of vibrational degrees of freedom is in the range 1–3 kK. This means that for efficient excitation of vibrations, the average electron energy should be higher (in air, it should be in the range 0.2–2 eV). Excitation of electronic degrees of freedom and gas dissociation require energies of 3–10 eV. If the average electron energy exceeds 10 eV, the main process in the plasma is gas ionization. Thus, the potential to control the energy of electrons suggests the potential for control of the direction of energy deposition and for the selective excitation of different degrees of freedom of the gas.

The average electron energy in a gas discharge is determined by a reduced electric field \( E/n \), where \( E \) is the electric field and \( n \) is the gas density. The critical \( E/n \) for a non-equilibrium electron energy distribution function (EEDF) formation is close to \( E/n \sim 0.1 \) Td for atomic gases and \( E/n \sim 1 \) Td for molecular gases (1 Td = \( 10^{-17} \) V cm\(^2\)). A non-equilibrium EEDF can be found as a solution of Boltzmann’s equation. In the simplest case, one can approximate the solution by a local, steady-state function that depends on the local electrical field only [24]. Further simplification is possible using the so-called two-term approximation (the electron distribution function is presented in the form \( f(v) = f_0(v) + f_1(v) \cos \theta \) [25], with \( v \) being the electron velocity and \( \theta \) being the angle between \( v \) and \( E \)) using a full set of cross sections for electron–molecule collisions.
The EEDF that is obtained allows calculation of the energy branching through the different degrees of freedom. Figure 1a demonstrates the energy branching through internal degrees of freedom of the gas for different $E/n$ values in a discharge. Rotational excitation dominates at very low $E/n \sim 0.1$ Td. Fast energy exchange between rotational and translational (RT) degrees of freedom leads to thermal-equilibrium gas heating in this type of discharge. An increase in the $E/n$ value to 0.4 Td changes the energetic priorities. Above this point, the main channel of electron energy losses becomes the vibrational excitation of oxygen. For a reduced electric field value in the interval $4 \text{Td} < E/n < 110 \text{Td}$ in air, the most efficient channel of electron energy losses is an excitation of the vibrational levels of nitrogen. Vibrational–translational (VT) relaxation under low-temperature conditions is a rather slow process, and the vibrational temperature in the discharge could be higher than the translational temperature. In the same region of $E/n$ values, the excitation of the lowest electronic level of oxygen, $O(a^1\Delta)$ state, takes place. The efficiency of this electronic excitation in the presence of nitrogen is very small (approx. 2%), but the low rate of singlet oxygen quenching under some conditions leads to an increase in the concentration.

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It should be noted that an electric field value of \( E/n \sim 120 \text{Td} \) is a very important threshold in air. Above this point, the electric field is enough to ionize the gas, and discharge can propagate in the self-sustained regime. Below this value, discharge can exist only in the presence of an external source of ionization. At an \( E/n \) from 140 to 500 Td, the main channel of energy losses is excitation of the electronic triplet states of nitrogen. Because of the high electron energy in this range of \( E/n \) (from 3 to 10 eV, respectively), ionization of the gas in the discharge gap is very fast. Between 500 and 1000 Td, the excitation of nitrogen singlet states becomes most significant, and above 1000 Td, the main portion of the electron energy goes to ionization of the gas.

Fuel additives (figure 1b–d) do not change this picture dramatically. The main reason is the relatively small concentration of fuel molecules in the mixture under typical combustion conditions. Figure 1b demonstrates the effect of hydrogen on the electron energy branching. A stoichiometric mixture H\(_2\)-air (H\(_2\):O\(_2\):N\(_2\) = 29:14.5:56.5) contains approximately 30 per cent hydrogen. It is clear from the calculations that these additives only change the energy branching slightly at moderate and high \( E/n > 20 \text{Td} \). The excitation of molecular nitrogen remains the main process. Vibrational and electronic excitation and ionization of hydrogen only change the energy branching slightly (figure 1b). At low \( E/n < 10 \text{Td} \), the influence of hydrogen addition becomes more significant. Vibrational excitation of hydrogen is the main channel of energy losses for \( E/n = 5–10 \text{Td} \). The role of the rotational excitation of hydrogen is also important and increases the energy flux into RT degrees of freedom under low \( E/n \) (figure 1b). Almost the same picture appears with the hydrocarbon fuels methane (figure 1c) and ethane (figure 1d).

Thus, for plasma-assisted combustion, we have a new, extremely important parameter—the reduced electric field in the discharge. The \( E/n \) value controls the direction of energy deposition in plasma and the composition of active particles in the discharge. Excited particles are quenched in relaxation processes to heat the gas, the effect that is important to plasma-assisted ignition.

(b) Non-equilibrium plasma recombination and relaxation

(i) Rotational relaxation

Let us consider briefly various relaxation mechanisms. Due to fast RT relaxation, the rotational degrees of freedom of the molecules are quenched rapidly. This process requires few collisions only. For example, for rotational relaxation in air \( \text{O}_2(\text{rot}) + M \rightarrow \text{O}_2 + M \) and \( \text{N}_2(\text{rot}) + M \rightarrow \text{N}_2 + M \), the typical relaxation time is comparable to the gas-kinetics time. This means that the typical time of rotational state thermalization is \( \tau \sim 0.5 \text{ ns} \) under normal conditions. This is why rotationally excited molecules cannot be considered to be active particles for non-thermal acceleration of chemical reactions. Another important point is that the energy of excitation of rotational states is very small (roughly equal to the translational temperature) and is significantly lower than the typical chemical reaction thresholds. However, it is possible to heat the gas through excitation of the rotational degrees of freedom.

(ii) Vibrational relaxation

In contrast to rotational state relaxation, quenching of the vibrationally excited states of \( \text{N}_2 \) and \( \text{O}_2 \) (VT relaxation) is a very slow process. The VT relaxation
time is usually longer than the typical time of plasma-assisted ignition (approx. 10–100 μs). These times become comparable when significant amounts of H2 or hydrocarbons are represented in the mixture. This means that vibrationally excited N2 and O2 molecules can accumulate in the discharge with intermediate $E/n$ values. Let us analyse the possibility of chemical reaction acceleration by vibrationally excited reagents. Non-equilibrium vibrational excitation of reagents can significantly accelerate reactions if a thermally equilibrium reaction path includes a significant energy barrier [26].

The influence of vibrational excitation is limited by VT relaxation of the molecules. This process becomes extremely fast in the presence of hydrocarbons. In mixtures with hydrogen, the efficiency of vibrational excitation increases because of the relatively slow vibrational relaxation of H2. An analysis by Zatsepin et al. [27] has shown that the oxidation rate increases in a H2–air mixture at $T = 300$ K by 3–5 times.

As an example of the possible applications of vibrational excitation of the flow, we refer to Bezgin et al. [28]. The peculiarities of an oblique detonation wave formation in a supersonic hydrogen–oxygen mixture flow over a plane wedge were numerically analysed. Preliminary excitation of molecular vibrations of H2 was shown to lead to a noticeable decrease in the induction-zone length and the distance at which the detonation wave was formed. It was demonstrated that the reason for these effects was an intensification of chain reactions in the H2–O2 (air) mixture, owing to the presence of vibrationally excited hydrogen molecules in the flow [28].

(iii) Electronic level excitation and relaxation

At $E/n \sim 100–500$ Td, the main channel of gas excitation is the population of the electronic degrees of freedom by electron impact and by energy exchange between vibrationally excited states. An important exception to this rule is the singlet state of molecular oxygen O2(a1$\Delta_g$). This state has a low excitation threshold and long radiative lifetime; the maximum efficiency of its population corresponds to $E/n \sim 3–10$ Td.

There are a number of different electronically excited particles in low-temperature plasma. Unfortunately, the reaction rate constants, quenching rates and products are known only for a limited number of these excited states. This is why we mention the most important levels here from the point of view of plasma-assisted combustion only.

The energy efficiency of electronic-state usage for plasma chemistry depends on the ratio between channels of depopulation of a state. For example, if the radiative lifetime of the state is too short, there will be some photon flux, but no reactions with this state. The collisional quenching efficiency depends on the products of the reaction. Quenching of the triplet states of nitrogen molecules by molecular oxygen leads to oxygen dissociation and atomic oxygen production. Another example is the quenching of singlet oxygen molecules by hydrogen or hydrocarbons, which mostly leads to heat release without the formation of active radicals.

The most important reactions with electronically excited molecules from the point of view of plasma-assisted combustion are channels that lead to radical
formation. There are different ways to produce radicals through excitation of electronic states.

(I) Excitation of the molecular electronic state and radical production in chemical reactions:

\[ \text{O}_2 + e \rightarrow \text{O}_2(a^1\Delta_g) + e \quad \text{O}_2(a^1\Delta_g) + \text{H} \rightarrow \text{O}^3\text{P} + \text{OH} \]
\[ \text{O}_2 + e \rightarrow \text{O}_2(b^1\Sigma^+_g) + e \quad \text{O}_2(b^1\Sigma^+_g) + \text{H}_2 \rightarrow \text{OH} + \text{OH} \]
\[ \text{N}_2 + e \rightarrow \text{N}_2(A^3\Sigma^+_u) + e \quad \text{N}_2(A^3\Sigma^+_u) + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}^3\text{P} \]

(II) Excitation of the molecule to repulsive or pre-dissociative term leads to molecule dissociation and the formation of two radicals:

\[ \text{O}_2 + e \rightarrow \text{O}_2(B^3\Sigma^−_u) + e \quad \text{O}_2(B^3\Sigma^−_u) \rightarrow \text{O}^3\text{P} + \text{O}(1\text{D}) \]
\[ \text{O}_2 + e \rightarrow \text{O}_2(C^3\Delta_u) + e \quad \text{O}_2(C^3\Delta_u) \rightarrow \text{O}^3\text{P} + \text{O}^3\text{P} \]
\[ \text{N}_2 + e \rightarrow \text{H}_2(a^3\Sigma^+_g) + e \quad \text{H}_2(a^3\Sigma^+_g) \rightarrow \text{H}(1\text{S}) + \text{H}(1\text{S}) \]

(III) Excitation of the molecule and dissociative quenching of an excited state by another molecule:

\[ \text{N}_2 + e \rightarrow \text{N}_2(C^3\Pi_u) + e \quad \text{N}_2(C^3\Pi_u) + \text{O}_2 \rightarrow \text{N}_2 + \text{O}^3\text{P} + \text{O}(1\text{D}) \]
\[ \text{N}_2 + e \rightarrow \text{N}_2(C^3\Pi_u) + e \quad \text{N}_2(C^3\Pi_u) + \text{H}_2 \rightarrow \text{N}_2 + \text{H}(1\text{S}) + \text{H}(1\text{S}) \]
\[ \text{O}_2 + e \rightarrow \text{O}_2(A^3\Sigma^+_u) + e \quad \text{O}_2(A^3\Sigma^+_u) + \text{C}_x\text{H}_y \rightarrow \text{O}_2 + \text{C}_x\text{H}_{y-1} + \text{H}(1\text{S}) \]

(IV) Excitation of the molecular electronic state with radiative depopulation, high-energy photon flux generation and dissociation (ionization) of gas molecules by this radiation:

\[ \text{N}_2 + e \rightarrow \text{N}_2(b^1\Pi_u) + e \quad \text{N}_2(b^1\Pi_u) \rightarrow \text{N}_2 + \text{h}v \quad \text{O}_2 + \text{h}v \rightarrow \text{O}_2^+ + e \]
\[ \text{N}_2 + e \rightarrow \text{N}_2(b^1\Pi_u) + e \quad \text{N}_2(b^1\Pi_u) \rightarrow \text{N}_2 + \text{h}v \quad \text{CH}_4 + \text{h}v \rightarrow \text{CH}_3 + \text{H} \]
\[ \text{H}_2 + e \rightarrow \text{H}_2(a^3\Sigma^+_g) + e \quad \text{H}_2(a^3\Sigma^+_g) \rightarrow \text{H}_2(b^3\Sigma_g) + \text{h}v \quad \text{O}_2 + \text{h}v \rightarrow \text{O} + \text{O} \]

Comprehensive, detailed kinetic models have been discussed for \( \text{N}_2–\text{O}_2 \) mixtures [29], for \( \text{H}_2–\text{O}_2–\text{N}_2 \) mixtures [27] and for \( \text{C}_x\text{H}_y–\text{O}_2 \) mixtures [30]. It should be noted however, that channel branching, rate coefficients and even the products of such reactions are not very well known. The first group of processes has been investigated much more thoroughly than the second and third groups. The simultaneous presence in the plasma of all sorts of excited particles and radicals makes detailed kinetic analysis an extremely challenging and resource-consuming task. As an example, mixture composition variation, a very popular approach in combustion chemistry, will not work in plasma chemistry because the EEDF in the discharge phase and the kinetics of gas excitation will change simultaneously with the afterglow kinetics variation.

Mechanism (I) requires a very low electric field to increase the efficiency of the excitation process because of the low energy threshold for oxygen singlet-state population. On the contrary, mechanisms (II)–(IV) require a high \( E/n \) value and high electron energy for upper electronic-state excitation.
It should be mentioned that the kinetic model of active particles formation in the discharge used by Kosarev et al. [31] and Aleksandrov et al. [32] is significantly simplified, and the rate coefficients of the number of processes are not very well known. This fact is related to the ion composition and in part to the composition of hydrocarbon radicals. Fortunately, under conditions of typical lean mixture combustion, atomic oxygen always plays a major role. Atomic hydrogen and hydrocarbon radicals are less important, but the processes of their formation are also well investigated and could be modelled with rather high accuracy. Uncertainty in the relative composition of radicals is not of critical importance under such conditions because the ignition delay time and the rate of chemical energy release at high temperatures do not significantly depend on the nature of the radical [32]. Thus, even plasma chemical systems are very complex, and some processes have not investigated in detail at the moment. Plasma-assisted ignition and combustion at high temperatures are controlled by rather simple and well-understood mechanisms and radicals.

(c) Vacuum ultraviolet emission of the discharge

It is well known that both equilibrium and non-equilibrium plasmas are strong sources of vacuum ultraviolet radiation (VUV). The absorption of VUV radiation by oxygen leads to molecular oxygen dissociation with a quantum efficiency close to one. Thus, ultraviolet sources can potentially generate high concentrations of active radicals in the gas.

The potential to use discharge VUV self-emission for ignition stimulation has been considered [33]. Pulsed microwave radiation was generated by a MI-389 magnetron. The radiation parameters were the following: a peak power of $P_i \leq 400$ kW, a pulse duration of $\tau_f \leq 50$ ms, a wavelength of $\lambda_f \sim 2.5$ cm, and a repetition frequency of $f \sim 10$ Hz. It was shown that, both in hydrogen–oxygen and in methane–oxygen media, non-self-sustained discharge initiated the primary combustion wave with relatively low temperatures and low glow intensities. Contrary to the data in the literature, the experiments did not show a significant difference between the propagation velocities of combustion waves in hydrogen- and methane-containing media, and considerable temperature jumps (above 1000 K) were observed behind the front of the primary wave. After the primary wave started from the initiator and passed some distance, a bright burst occurred rapidly and almost simultaneously throughout the region under observation. This burst is characteristic of the transition to explosive combustion of a gas mixture. The observed specifics of the initiation and propagation of the combustion are attributable to both ‘gas dynamic’ and ‘kinetic’ mechanisms (in particular, to the action of ultraviolet radiation on the gas medium; the source of radiation was numerous sparks arising at metal–dielectric contacts at the target surface irradiated with the microwave beam).

It should be mentioned that the excitation of upper states with typical thresholds of 10–15 eV requires significant energy. The energy cost per radical in this case becomes comparable or even higher than that for the ionization channel. This is why VUV radiation cannot be considered as a primary channel of mixture excitation. However, radiation can propagate through the gas and de-localize the discharge excitation.
(d) Role of gas ionization and plasma recombination in plasma-assisted combustion

Ionization is a highly energy-intensive process. The best results can be achieved using an electron beam with an energy above 1 keV (approx. 34 eV per ion in air). Gas discharges at extremely high overvoltages operate in the same mode, generating a flux of run-away electrons with an energy close to the applied voltage [34]. Gas discharge in the form of a fast ionization wave, developing at \( E/n \sim 1000 \text{Td} \), has approximately twice as low efficiency as an electron–ion pair production (approx. 65 eV per ion). Gas discharges with lower overvoltages (\( E/n \sim 100 \text{Td} \) for streamers, glow discharges) have a very low efficiency of gas ionization.

Another important point regarding gas ionization is fast plasma recombination. This process is discussed in detail elsewhere [32,35]. Even for an electron concentration of \( n_e \sim 10^{12} \text{cm}^{-3} \), the recombination time at \( T \sim 300 \text{K} \) is less than 1 \( \mu \text{s} \) because of cluster ion formation and at \( T \sim 3000 \text{K} \), is an order of magnitude longer (approx. 10 \( \mu \text{s} \), molecular ion–electron recombination mechanisms). Fast energy redistribution across different degrees of freedom (energy thermalization) leads to effective gas heating on a microsecond time scale [32]. The combination of these two factors—very high energy cost of ionization and very high rate of recombination—makes ionization ineffective from the point of view of plasma-assisted combustion. Other researchers [36,37] have shown that the efficiency of radical production in air–fuel mixtures has a maximum at \( E/n \sim 200–400 \text{Td} \). A further increase in the electrical field value led to a shift in the discharge energy branching to gas ionization and increased the cost of radical production.

Of course, a detailed analysis of the efficiency of gas ionization on the ignition process should take into account the gas composition, temperature, pressure and plasma density. For example, for a high concentration of electrons, the main process of plasma recombination is electron–ion dissociative recombination [32]:

\[
\begin{align*}
N_2^+ + e &\rightarrow N(4S) + N(4S, 2D) \\
O_2^+ + e &\rightarrow O(3P) + O(3P, 1D)
\end{align*}
\]

Another scenario of ion influence on the oxidation and combustion processes is ionic oxidation chain formation [38,39].

An ionic mechanism associated with charge transfer in a \( \text{H}_2–\text{O}_2 \) system was proposed [39]:

\[
\begin{align*}
\text{O}_2 + e^- + \text{M} &\rightarrow \text{O}_2^- + \text{M} \\
\text{H}_2 + \text{O}_2^- &\rightarrow \text{OH}^- + \text{OH} \\
\text{OH} + \text{H}_2 &\rightarrow \text{H}_2\text{O} + \text{H} \\
\text{OH}^- + \text{H} &\rightarrow \text{H}_2\text{O} + e^- \\
\text{H} + \text{O}_2 + \text{M} &\rightarrow \text{HO}_2 + \text{M} \\
\text{OH}^- + \text{HO}_2 &\rightarrow \text{H}_2\text{O} + \text{O}_2 + e^-
\end{align*}
\]

Thus, gas ionization plays two roles during plasma decay. Recombination can lead to the formation of molecules and significant heat release to translational degrees of freedom. A competing mechanism is the recombination with radical (atoms)
formation or excited-particle formation. This mechanism produces less heat but more active radicals in the discharge afterglow. Overall, ionization produces more thermal heat and fewer radicals than the excitation of the electronic degrees of freedom of nitrogen and the direct dissociation by electron impact \[35\]; thus, it is not very effective from the point of view of active radical formation because of the relatively high energy cost per radical.

*(e) Fast gas heating*

Energy release during plasma decay increases the gas temperature and helps us to initiate the chemical reaction. The key issue is the rate of energy release. A long relaxation time leads to an energy ‘freeze’ in the chemical or internal degrees of freedom. Thus, we should compare the time scale of ignition delay with the time scale of energy thermalization. The dynamics of plasma relaxation in the case of excitation by low and moderate electrical fields have been calculated many times (e.g. \[40\]).

A well-known mechanism for heating molecular gases is the relaxation of vibrationally excited molecules, which form a reservoir of energy in discharge plasmas. This process takes a sufficiently long time. Channels of fast (1 μs or faster at atmospheric pressure) heating in air, molecular nitrogen and other gases have received considerable interest in the past two decades (see \[41\] and references therein). In low (<20 Td) reduced electric fields, \(E/n\), the contribution to fast electrical energy dissipation is controlled by elastic collisions between electrons and neutral particles, as well as by rotational excitation of molecules by electron impact followed by RT relaxation. At higher values of \(E/n\), the fraction of electron energy transferred to heat owing to elastic collisions and rotational excitation is less than 3 per cent. This result disagrees with a number of observations in molecular nitrogen, air and other \(\text{N}_2\):\(\text{O}_2\) mixtures, in which the fractional electron power transferred quickly to heat has been found to be as large as 10–15% for \(E/n > 80\) Td (see \[41\] and references therein). Here, the mechanism of fast gas heating in pure nitrogen was assigned to self-quenching reactions of the \(\text{N}_2(\text{A}^3\Sigma_u^+)\) state. In air and in other \(\text{N}_2\):\(\text{O}_2\) mixtures, fast gas heating was explained by electron-impact dissociation of \(\text{O}_2\), by quenching of electronically excited \(\text{N}_2\) states in collisions with \(\text{O}_2\), and by quenching of the \(\text{O}(1\text{D})\) state \[41\]. Computer simulations showed that the fractional electron power transferred quickly to heat increased with an increasing electric field. This is due to a growth in the electron energy fraction that is spent on the excitation and dissociation of \(\text{N}_2\) and \(\text{O}_2\) molecules \[40,41\]. The calculated results could be approximated by the assumption that 28 per cent of the energy spent on the excitation of electronic \(\text{N}_2\) and \(\text{O}_2\) states is quickly transferred to heat \[41\].

The model \[35\] of fast gas heating takes into account the mechanisms of energy release suggested by Popov \[41\] to describe observations at moderate values of \(E/n\). In addition, it considers the channels associated with the excitation of higher excited states of the molecules and with the formation, transformation and recombination of charged particles, which are the processes that become important at high values of \(E/n\). How the released energy is shared between the products is unknown for most of the ion–molecule reactions. In these cases, it was assumed that all the released energy was transferred to gas heating for the following reasons \[35\]. First, the energy stored in vibrational ion states after the
reactions is known to be transferred to the translational degrees of freedom of the molecules (VT relaxation) with high ($\sim 10^{-10}$ cm$^3$ s$^{-1}$) rates (see [42–45] and references therein). The characteristic time of gas heating at atmospheric pressure here is around 0.1–1 ns. Second, the vibrational excitation of neutral molecules was neglected because it is generally not very high, and, consequently, the effect of gas heating was somewhat overestimated in this case.

Thus, the analysis of discharge processes shows that the discharge energy can be deposited into the desired internal degrees of freedom of molecules when varying the reduced electric field, $E/n$, at which the discharge is maintained. The amount of the deposited energy is controlled by other discharge and gas parameters, including the electric pulse duration, discharge current, gas number density, gas temperature, etc. As a rule, the dominant mechanism of the effect of non-equilibrium plasma on ignition and combustion is associated with the generation of active particles in the discharge plasma. Numerical simulation of discharge processes is based on the solution of the Boltzmann equation for electrons and of the balance equations for active particles. Here, the input data are electron–molecule cross sections and rate constants for reactions with excited and charged particles. These data are available for simple molecules, such as N$_2$, O$_2$, H$_2$, and, to a smaller extent, for simple hydrocarbons. However, little is known about the cross sections and rates for complex hydrocarbon molecules. The lack of this information does not seem critical when considering lean and stoichiometric mixtures, but this problem becomes serious in simulation of the ignition of rich mixtures.

For plasma-assisted ignition and combustion in mixtures containing air, the most promising active species are O atoms and, to a smaller extent, some other neutral atoms and radicals. These active particles are efficiently produced in high-voltage, nanosecond pulse discharges owing to electron-impact dissociation of molecules and owing to electron-impact excitation of N$_2$ electronic states followed by collisional quenching of these states to dissociate the molecules. This mechanism was validated above the self-ignition threshold for lean and stoichiometric, fuel–oxygen and fuel–air mixtures at pressures up to 2 atm. It was shown that, in a wide range of conditions, the optimal $E/n$ from the point of view of atomic oxygen generation was approximately twice as high as the electrical breakdown threshold of the mixture. Excitation of the low-energy singlet states of O$_2$ could be efficient in pure oxygen. However, fast quenching of oxygen singlets by fuel molecules (hydrogen, hydrocarbons) significantly decreased the efficiency of this channel. The addition of N$_2$ led to a smaller amount of energy spent on the excitation of these states because of the competition with vibrational excitation of N$_2$.

Vibrationally excited particles accelerate the reactions and the rate of energy release. This mechanism becomes very important under low-temperature conditions, in which the reaction-energy thresholds cannot be overcome using translational energy only. A competing process is VT relaxation of the gas, which reduces the chances of long energy-back-coupling chain development.

Generation of charged particles in discharge plasmas seems to be inefficient for favouring ignition because the energy cost of ionization is too high and because the lifetime of charged particles is too short. Despite this fact, ionization and fast plasma recombination remains an important channel of fast volumetric gas heating and can be used for plasma-assisted ignition.

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The major problems with the physical and chemical models of plasma-assisted combustion are associated with the low-temperature regimes below the self-ignition threshold. For this range of parameters, there are no validated combustion mechanisms. The uncertainties associated with attempts to extrapolate high-temperature combustion mechanisms to low temperatures are too large. A new, validated mechanism for low-temperature hydrocarbon combustion is required for a qualitative description of plasma-assisted combustion below the self-ignition threshold. This problem is still unsolved and requires a lot efforts.

3. Plasma-assisted ignition and deflagration-to-detonation transition control

The studies of different mechanisms of detonation initiation in combustible gaseous mixtures are related to the necessity of developing an ignition device for application in PDEs. This application requires a robust, energy-efficient method of initiation of CJ detonations in tubes within distances of several calibres and times of approximately 1 ms. The most common approach is DDT facilitation by the application of various types of obstacles that make the flow turbulent and increase the flame velocity, which was initially suggested by Shchelkin [46].

Alternatively, Oppenheim & Urtiew [47] illustrated the coupling between an overdriven shock and a reaction zone—the classic ‘explosion in an explosion’ phenomena—in 1966. The concept of detonation initiation through a gradient mechanism was theoretically introduced by Zeldovich et al. [48]. According to this work, an ignition delay time (or induction time) gradient that is formed owing to a corresponding temperature gradient leads to the onset of a spontaneous combustion wave. The mixture first ignites at the point with the lowest delay and then propagates by spontaneous ignition with a velocity $D_{sp}$ determined by the shape of the gradient. Depending on the value of $D_{sp}$, different modes of flame propagation can be realized.

— When $D_{sp}$ exceeds the CJ velocity $D_{CJ}$, an energy release occurs almost simultaneously in the vicinity of the initiation point. A detonation wave can emerge from this near-homogeneous explosion as a spontaneous wave, which decelerates to the $D_{CJ}$ velocity.

— When $D_{sp}$ falls into the interval between the speed of sound and $D_{CJ}$, a spontaneous wave propagating over the induction time gradient can become coupled with a compression wave and thus evolve into a detonation wave through shock amplification and acceleration.

A similar concept of shock-wave amplification by coherent energy release (SWACER) was introduced by Lee et al. [17] and was investigated in more detail. Recently, this problem was numerically studied in a series of papers reviewed by Oran & Gamezo [49], in which the detonation wave always occurred from a hot spot in the region between the shock wave and the turbulent flame. Various scenarios of hot-spot formation owing to shock–flame interactions and the role of hot spots were also discussed.
Plasma-assisted ignition and DDT

(a) General configuration of a TPI interface. (b) Streamer formation [22]. HV DC, high-voltage direct current. Reproduced with permission. (Online version in colour.)

(a) Deflagration-to-detonation transition by radial plasma filaments

Experiments to determine the effectiveness of a transient plasma for initiating a detonation in a short tube with radial propagation of the streamers were carried out by Gundersen and co-workers [15,22,50–53].

The interface between the transient-plasma ignition (TPI) system and the PDE was largely the same for the various experiments (figure 2). A typical electrode was a rod threaded for field enhancement to assist in streamer development. The rod was about 12 cm in length and acted as the anode, running coaxially in the centre of the tube at the engine head [22].

A TPI system has been demonstrated to substantially reduce the ignition delay and DDT times for ethylene–air and propane–air mixtures for a temperature range of 280 to 430 K and pressure range of 1 to 6 atm. Ignition delays were reduced by up to a factor of five, and the corresponding DDT time scales were observed to decrease accordingly when compared to conventional capacitive discharge systems. The substantial reduction in the ignition delay times resulted in the generation of strong pressure waves that inherently steepened into shock waves quickly and in a short distance. Although direct initiation of a detonation wave was not obtained, the subsequent use of a Shchelkin spiral was able to rapidly and reliably accelerate the combustion-driven shock waves to detonations within practical distances [22].

(i) Transient-plasma ignition

TPI, involving short ignition pulses (typically 10–50 ns), has been shown to effectively reduce ignition delays. Two distinct phases of the plasma-ignition process have been observed: an initial non-equilibrium plasma phase, wherein energetic electrons transfer energy to electronically excited species that accelerate reaction rates, and a spatially distributed thermal phase, which produces
Figure 3. (a) Streamers generated by a single 370 mJ, 56 kV, 54 ns pulse (maximum \( E/n \approx 400 \) Td) in air (10 s gate time). (b) Flame propagation from multiple ignition sites at the base of the streamers after a single pulse in \( \varphi = 1.1 \) C\(_2\)H\(_4\)–air (1 ms gate time). Both images were captured from the same off-axis angle [53]. Reproduced with permission. (Online version in colour.)

Exothermic fuel oxidation reactions that result in ignition. It was shown that ignition kernels were formed at the ends of the spatially separated streamer channels and at the cathode and/or anode depending on the local electric field strength, and that the temperature in the streamer channel was close to room temperature up to 100 ns after the discharge [53].

The results presented in figure 3 show that after a transient-plasma discharge in \( \varphi = 1.1 \) C\(_2\)H\(_4\)–air at 1 atm: (i) ignition occurred within the streamer channel, (ii) flame initiation occurred within 1 ms of the discharge, and (iii) flame propagation was faster than when initiated by conventional spark ignition. Therefore, when considering the mechanism of ignition via transient-plasma discharge, it is relevant to consider how the energy is deposited, over what time scale, and how that impacts ignition. Approximately 1.5 mJ was applied to the fuel–air mixture in each streamer, which was sufficient for ignition [53].

Although the TPI strategy provides an accelerated combustion sequence leading to the rapid generation of strong pressure waves, the shock ultimately generated by the expanding combustion products must still be accelerated by conventional means (figure 4 [50]). Detonations were successfully obtained for stoichiometric and fuel-rich ethylene–air mixtures when wall turbulence was introduced after the ignition chamber through the use of a spiral. It has been demonstrated that pulsed distributed discharge systems are better than conventional capacitive discharge spark systems because they provide a stronger initial ignition source while consuming comparable energy, which results in reducing the characteristic ignition delay and subsequent DDT time by at least a factor of three [50].

(b) Transient-plasma deflagration-to-detonation transition

Experiments have been carried out to determine the effectiveness of a transient plasma, i.e. corona discharge, to initiate a detonation in a short tube [15]. A high-voltage pulse generator equipped with a pseudo-spark switch was used.
Figure 4. (a) The peak pressure at room temperature (288 K) for C$_2$H$_4$–air mixture ($\varphi = 1.2$) for the TPI system (open squares, with Shchelkin spiral; filled circles, without Shchelkin spiral). (b) Ignition delay time versus temperature for C$_2$H$_4$–air mixture ($\varphi = 1.44$) after both capacitive engines [50] (filled squares, converted spark plug (200 mJ); asterisks, transient plasma (300 mJ)).

to discharge a capacitor through a transformer connected to electrodes in the combustion initiator section. The resulting voltage pulse (90 kV for 50 ns) produced a plasma discharge consisting of many radial streamers. The transient plasma initiated low-speed combustion, a deflagration, which can undergo transition to detonation if the mixture is sufficiently sensitive. Corona discharge was an excellent method to achieve very rapid combustion of the region near the electrodes, but additional means appeared to be needed to accelerate the resulting flame to detonation for mixtures with greater than 40 per cent nitrogen dilution.

Figure 5a, b shows images of streamers in a corona discharge and an arc in spark discharge, respectively. A sequence of chemiluminescence images is shown in figure 5c. The images depict the plasma initiation process of a methane–air mixture with $\varphi = 0.7$. This experiment was carried out at 1 atm initial pressure and 298 K initial temperature. The camera had a 0.0166 s exposure time and a 0.033 s interframing time. The combustion front was determined to propagate radially from the axis to the walls of the initiator chamber with a mean radial velocity of 0.61 ± 0.08 ms$^{-1}$ (figure 6).

It has been demonstrated that non-thermal ignitions can reduce the ignition delay by 5–6 ms (30–45%) below that observed with an aftermarket automotive ignition at lean to stoichiometric fuel–air equivalence ratios, using an experimental PDE fuelled with aviation gasoline [52]. Non-thermal ignitions with 0.5–3 J energies produced the shortest ignition delays. Ignition delays were approximately the same for positive corona or negative spark discharges. It has also been demonstrated that by a simple modification of an aftermarket automotive thermal ignition, the ignition delays could be reduced by 4 ms under the same PDE operating conditions but with 0.115 J exciter energy. The shortest ignition delay at $\varphi = 1$ was 6 ms, produced by TPI. At $\varphi = 0.8$, an ignition delay of 11 ms was observed with both the transverse exciter (TE) and the TPI. Ignition delays were substantially longer than the DDT times, which were approximately 1–3 ms.
Figure 5. (a) An image of streamers during a pulsed corona discharge. (b) An image of an arc from a spark discharge. The arc is formed between a needle on the centre electrode and the bottom wall of the initiator. (c) A sequence of chemiluminescence images, viewing axially down the tube, showing the initiation of a combustion front. The mixture is methane–air with $\phi = 0.7$ at a standard temperature and pressure [22]. Reproduced with permission. (Online version in colour.)

![Figure 5](image)

Figure 6. (a) Ignition delay versus % N$_2$ dilution for the various ignition configurations. (b) Ignition delay and DDT time versus % N$_2$ dilution for the various ignition configurations [22]. SP, spark discharge; PI, plasma ignition. Reproduced with permission. (Online version in colour.)

![Figure 6](image)

Ignition delay and DDT data for a TE ignition that produces positive polarity pulses and the modified multiple spark discharge (MSD) ignition are shown in figure 7. A surface discharge igniter was used with both ignitions. The PDE was fuelled with aviation gasoline. The energy levels quoted in the figure are estimated exciter energies. All of the TE ignition delay curves lie below the baseline MSD ignition delay curve. As the capacitance and energy increased, the ignition delay decreased, while the DDT times remained approximately constant. The shortest ignition delays were 6.5 ms at $\phi = 1$ and 1.2 and 11 ms at $\phi = 0.8$ when a 4 nF capacitor was installed in the TE. The spread from the lowest capacitance (130 pF) to the highest capacitance (4 nF) was 1.5 ms at $\phi = 1$ and 1.2 and 5 ms at $\phi = 0.8$. A comparison between the TE ignition delays at two
selected capacitances and the modified and unmodified MSD ignition delays was performed. The modified MSD ignition delays were comparable to those of the TE ignition, although the exciter energy of the modified MSD ignition was less. The data indicate that a thermal (modified MSD) ignition can produce ignition delays comparable to those of a non-thermal (TE) ignition for radial configuration of the discharge development.

(c) Deflagration-to-detonation transition by longitudinal plasma filaments

An experimental demonstration of a longitudinal, high-voltage, nanosecond, gas-discharge application for initiation of detonation was proposed by Starikovskii [37] and performed by Starikovskiy and co-workers [21,54–61].

(i) Deflagration-to-detonation transition in multi-electrode system

Discharge formation

An experimental demonstration of the application of a longitudinal, high-voltage, nanosecond gas discharge for initiation of detonation was performed [21]. A pulsed, nanosecond discharge initiated detonation at a DDT length of up to 130 mm in a tube with a diameter of 140 mm. The detonation was initiated by an energy of 70 mJ in a C_3H_8 + 5O_2 mixture at an initial pressure of 0.3 atm.
Figure 8. (a) Discharge section (side view). Discharge development (front view). Air, \( P = 0.3 \) atm. \( U = 70 \) kV. (b) \( t = 10 \) ns; (c) \( t = 16 \) ns; (d) \( t = 22 \) ns [21]. Reproduced with permission. (Online version in colour.)

Measurements of the minimal ignition energy and ignition delay time were performed in \( \text{C}_3\text{H}_8/\text{C}_4\text{H}_{10} + 5\text{O}_2 + x\text{N}_2 \) and \( 0.5\text{C}_6\text{H}_{14} + 5\text{O}_2 + x\text{N}_2 \) mixtures in a pressure range 0.15–0.6 atm. The discharge section was attached to the end-plate of the detonation tube. The discharge chamber consisted of 131 separated sections that had common high-voltage and grounded electrodes. The discharge provided uniform excitation at a length of 80 mm. In the experiments, the high-voltage electrodes were supplied with a positive pulse with an amplitude of 4–70 kV and duration at half-width of 50 ns. The calculated reduced electric field ranged from 300 to 7000 Td near the high-voltage electrode. The discharge development had three time stages (figure 8). During the first stage, the emission intensity rose sharply. In the second stage, the emission intensity decreased. The third stage is the afterglow stage. The durations of the first, second and third stages were approximately 10, 50 and 500 ns, respectively. The duration of the stages increased with initial pressure rise. The initial stage of the discharge (up to 10 ns) was spatially quasi-homogeneous.
Deflagration-to-detonation transition in a distributed system

An experimental study of ignition and detonation initiation by two different kinds of high-voltage, pulsed gas discharges has been performed in two smooth detonation tubes. The experiments were carried out at pressures ranging from 0.15 to 1 bar in various gaseous, stoichiometric mixtures (figure 9). In the first setup, a distributed, non-equilibrium, nanosecond discharge was used for mixture excitation and ignition. In the second setup, a localized, microsecond, pulsed spark discharge with a stored energy of 14 J was implemented.

The electrical parameters of the discharges, ignition delay time, flamefront and shock-wave velocities were measured in the experiments. Essentially, a higher efficiency of the nanosecond discharge in comparison to the microsecond one as a detonation initiator was demonstrated. The DDT was observed at three tube diameters away from the discharge chamber in different C$_3$H$_8$/C$_4$H$_{10}$ + 5O$_2$ + xN$_2$ and 0.5C$_6$H$_{14}$ + 5O$_2$ + xN$_2$ mixtures with nitrogen concentrations up to 38 per cent. The energy input in these cases did not exceed 3 J, and the DDT time was less than 1 ms. The microsecond spark discharge ignited the mixture efficiently, but the transition length and time increased significantly (figure 10).

(d) Deflagration-to-detonation transition in single discharge cell

To clarify the mechanism of DDT initiated by longitudinal discharge, an experimental study of detonation initiation in a stoichiometric propane–oxygen mixture by a high-voltage, nanosecond gas discharge was performed in a detonation tube with a single-cell discharge chamber. The discharge study performed in this geometry showed that three modes of discharge development were realized under the experimental conditions: a spark mode with high-temperature channel formation, a streamer mode with non-uniform
gas excitation, and a transient mode. Under spark and transient initiation, simultaneous ignition at all points in the discharge channel occurred, forming a shock wave and leading to a conventional DDT via an adiabatic explosion. The DDT length and time at 1 bar of initial pressure in the square, smooth tube with a 20 mm transverse size were 50 mm and 50 μs, respectively. The streamer mode of the discharge development at an initial pressure of 1 bar resulted in non-uniform mixture excitation and a successful DDT via a gradient mechanism, which was confirmed by high-speed, time-resolved intensified charge coupled device (ICCD) imaging. The gradient mechanism implied a longer DDT time of 150 μs, a DDT run-up distance of 50 mm, and an initiation energy of 1 J, which is two orders of magnitude less than the direct initiation energy for a planar detonation under these conditions.

A detonation tube with a single-cell discharge chamber and nanosecond initiation has been assembled (see the scheme in figure 11). The discharge cell was a Plexiglas cylinder with a coaxial cylindrical channel. The Plexiglas cylinder served as a dielectric barrier. A pin-like, high-voltage electrode was placed inside the channel with a diameter of 6.5 mm [61]. The grounded electrode was at the outlet of the channel. The cell was covered with a grounded shield. A narrow gap in the shield along the discharge cell axis made it possible to perform direct optical imaging of the processes occurring inside the channel. The discharge was initiated by a high-voltage pulse delivered to the electrode from a nitrogen-filled, Marx pulse generator with spark-gap commutators via a 50 Ω coaxial line. The high-voltage pulse was 50 ns at half-maximum; its amplitude could be varied from 80 to 160 kV.

Discharge development

The discharge development modes were studied with a Hamamatsu C5680 fast streak camera. The maximum available micro-channel plate gain of the camera was $5 \times 10^3$, and the spectral response was in the wavelength region between
200 and 800 nm. The streak camera sweep time could be varied from 5 ns to 1 ms. The discharge was initiated by a pulse of 80–90 kV formed by the Marx generator. The discharge gap was set to 150 mm. The discharge propagated from the positive high-voltage electrode on the left (0 on the x-axis) towards the ground electrode on the right (150 on the x-axis). In all cases, a streamer was seen propagating during the first 5–30 ns. The streamer velocity depended on the value of the reduced electric field, which varied with pressure in the experiments. Under sufficiently high values of the reduced electric field, the streamer reached the grounded electrode before the high-voltage pulse ended, which resulted in high-current channel formation and rapid gas heating throughout the volume of the discharge cell. When the reduced electric field was not high enough, the streamer could not reach the grounded electrode. In this case, distributed gas excitation took place. At a pressure of 0.3 bar in air, the spark mode was observed. The streamer propagated with a velocity of $13 \text{mm ns}^{-1}$ (figure 12). After it had reached the grounded electrode, a return stroke propagated backwards at a velocity exceeding that of the forward-propagating streamer. The return stroke formed an intensively emitting, high-current plasma channel.

At a higher air pressure of 1 bar, the streamer velocity ($3.5 \text{mm ns}^{-1}$) fell below the value necessary for gap closure. The incident high-voltage pulse was too short for the streamer to reach the grounded electrode (figure 13). No return stroke propagation and high-current channel formation were observed in the streamer mode. Instead, the gas was seen to be excited non-uniformly, forming an excited species concentration gradient along the discharge gap. As was shown above, ignition by the non-equilibrium plasma is mainly governed by atomic oxygen produced by the discharge and, to some extent, by fast gas heating owing to plasma decay. The shape of the O atom density gradient was estimated based on the emission intensity distribution [61].

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The result is presented in figure 13 in terms of a normalized O atom distribution along the interelectrode gap obtained by integrating the intensity over the discharge duration. It is seen that the gradient spans approximately 10 cm under these conditions. The absolute values of radical concentrations for the hydrocarbon–oxygen mixture were estimated using the two-term expansion of the Boltzmann equation. The calculation showed that 20 per cent of the pulse energy was transferred to translational degrees of freedom and approximately 60 per cent into gas dissociation. Taking into account the actual energy input and the total number of gas molecules, the discharge produced approximately 2 per cent O atoms, approximately 1 per cent H atoms and approximately 1 per cent C2H5 radicals. At the same time, the discharge heated the mixture by approximately 300 K on average.

Under certain experimental conditions, a transient initiation mode was observed. After the discharge initiated by the incident high-voltage pulse had developed in the streamer mode, the pulse was reflected off the gap, having lost 10–25% of its energy in gas ionization, dissociation and excitation. The pulse then travelled back towards the generator, where it was re-reflected again, losing a significant portion of its energy in the generator. After 500 ns, the pulse reached the gap for the second time. Under the experimental conditions (0.3–1 bar), this time period was not enough for complete plasma recombination; thus, the gas in the discharge channel remained partially ionized. This resulted in the development of the second discharge under lower reduced electric field (E/n) values and the formation of a relatively hot conducting channel. With this type of initiation, the energy of the discharge was partitioned between the translational and internal degrees of freedom of the gas, forming a typical transient plasma.

**Deflagration-to-detonation transition initiation by spark discharge**

The spark mode of discharge development was realized in the whole pressure range under a maximum pulse amplitude of 160 kV, which corresponded to a
Plasma-assisted ignition and DDT

Figure 14. $x$–$t$ diagram of DDT, spark mode. (a) Initial pressure of 0.3 bar; (b) initial pressure of 1 bar. Insert in (a) represents the ICCD image of ignition development in the discharge gap. Stoichiometric propane–oxygen mixture. (Online version in colour.)

pulse energy of 15 J. The discharge gap in the experiments at an initial pressure of 0.3 bar was 100 mm. This resulted in an energy input into the gas of approximately 10 J. Typical $x$–$t$ diagrams based on the pressure transducers (PT) and the infrared (IR) sensors are presented in figure 14. The time was counted from the moment the nanosecond discharge developed. The origin of the $x$-coordinate coincides with the grounded electrode of the discharge gap. The negative $x$-values correspond to the discharge channel and are used to represent the ignition process dynamics captured with ICCD cameras. Each data set in the positive $x$-values region corresponds to a pair of PT and IR sensors installed at different distances from the nozzle inlet. It is seen from the data that, during the first measurement section, the flamefront was closely coupled with the shock wave and propagated with a supersonic velocity of over 700 m s$^{-1}$. The temporal delay between the waves was approximately 10 μs, which yielded approximately 7 mm for the gap length. Assuming that the flamefront and the shock wave travelled at that velocity between the nozzle inlet and the first sensor, the propagation of the flamefront and shock wave occurred with nearly zero delay after the discharge. Such a pattern resulted in successful DDT between the third and the fourth sensors, 230 mm from the nozzle inlet, which was 11–12 transverse tube sizes. The average velocity in this region—2100 m s$^{-1}$—was slightly lower than the calculated CJ value. Also, a detonation wave was clearly seen propagating backwards with an average velocity of 1700 m s$^{-1}$. The DDT time did not exceed 300 μs.

The ignition process inside the discharge channel was studied with a LaVision Picostar HR 12 ICCD camera. One image with a 1 ns gate was taken during each experiment through an interference filter with a maximum transmittance at 431.1 nm and a full-width at half-maximum of 2.6 nm. The ICCD image taken 5 μs after the discharge is shown in the insert of figure 14. The image intensity corresponds to flame emission inside the discharge channel. The light line in the image designates the channel, with its high-voltage electrode on the left and the detonation tube on the right. It is seen that, 5 μs after the discharge, the mixture was already ignited over almost all the cell volume, which is represented by the horizontal dashed line in figure 14a. This implies simultaneous ignition of
the mixture in terms of the typical temporal scale of gas-dynamic processes and confirms the assumption that the propagation of both the flame and the shock wave occurred without a significant delay. After simultaneous ignition inside the cell, a DDT occurred in the detonation tube. It is seen that, in the early stages (0–200 $\mu$s), a deflagration wave propagated with a velocity of approximately 700 m s$^{-1}$, which agrees well with the sensor data. A detonation wave was formed less than 300 $\mu$s after the discharge. The spark mode of DDT initiation at an initial pressure of 1 bar resulted in a significantly shorter DDT time and run-up distance, though under the same energy input of 10 J from the high-voltage pulse (figure 14b). The corresponding $x$–$t$ diagram based on PT data is presented. The average velocity became equal to the CJ value between sensors 1 and 2, which implies that the detonation wave was formed before or shortly after sensor 1. Thus, the DDT time was 50 $\mu$s, and the run-up distance was 50 mm or less. Thus, it was shown that the ignition in the distributed spark mode led to a fast DDT, even in a smooth tube.

**Deflagration-to-detonation transition initiation by transient plasma**

At a pressure of 0.3 bar, the combined transient initiation mode was realized with a pulse amplitude of 80 kV and under a longer discharge gap of 150 mm. The energy of the pulse was 4–5 J, whereas the energy input in the initial streamer discharge was less than 1.5 J. The DDT pattern for this kind of initiation in terms of an $x$–$t$ diagram is shown in figure 15b. The initial velocity of the shock wave was 600 m s$^{-1}$, which is slightly lower than that for the spark initiation at the same initial pressure. During the initial stages, the flame followed the shock wave with the same velocity, but with a notable delay of 30–40 $\mu$s. The flame then accelerated and caught up with the shock wave shortly after sensor 3. The acceleration took more time and distance to occur in comparison with the spark mode. The average velocity between sensors 3 and 4 was only 1150 m s$^{-1}$. However, the DDT did occur between these sensors, because a detonation wave was clearly seen propagating backward from some point in that region. The DDT length and time were approximately 250 mm and 400 $\mu$s, respectively.

In order to realize this initiation mode at an initial pressure of 1 bar, the pulse amplitude was raised to 120 kV under the same interelectrode gap of 150 mm. The pulse energy was 12 J, 1.2 J of which was deposited in the plasma by the first streamer discharge. A significant portion of the pulse energy—over 3 J—was deposited during the second discharge. The $x$–$t$ diagram under these conditions is presented in figure 15b. At the higher pressure, the flame caught up with the shock wave sooner; the delay was only 10 $\mu$s at sensor 1, completely diminishing later on. The average velocity value corresponded to the CJ value between sensors 1 and 2. The DDT time was slightly over 60 $\mu$s, and the run-up distance was $\sim$50 mm, which are quite close to the values observed for the spark initiation under the same conditions.

**Deflagration-to-detonation transition initiation by streamer discharge: gradient mechanism**

The streamer mode of discharge development could be realized at a discharge gap of 150 mm, an initial pressure of 1 bar, and a pulse voltage of 80 kV. The pulse energy and the energy input were 4.5 and 1 J under these conditions, respectively.
Figure 15. (a) $x$–$t$ diagram of DDT at an initial pressure of 0.3 bar, transient initiation mode. (b) $x$–$t$ diagram of DDT at an initial pressure of 1 bar, transient initiation mode. Stoichiometric propane–oxygen mixture.

Figure 16. (a) $x$–$t$ diagram of DDT at an initial pressure of 1 bar, streamer mode. (b) Time-resolved ICCD imaging of fuel–mixture ignition inside the discharge chamber. DDT at an initial pressure of 1 bar, streamer mode. The discharge energy $W$ was 1 J. Stoichiometric propane–oxygen mixture. (Online version in colour.)

The secondary re-reflected pulse was too weak to produce any significant effect on the pre-ionized gas under these conditions. The streamer mode of discharge propagation without the formation of a hot channel resulted in a different DDT pattern. The results are presented in terms of an $x$–$t$ diagram and in terms of a time-resolved frame sequence captured with an UltraSpeedStar16 camera in figure 16. From the IR sensor data, the flamefront propagated at the CJ velocity between sensors 1 and 2, which is quite similar to the pattern observed at 1 bar under other initiation modes. However, the DDT time was significantly longer and amounted to 150 $\mu$s. At the same time, ICCD imaging showed that the ignition did not occur simultaneously over the channel. Instead, a flame was seen originating in the region closest to the high-voltage electrode after a delay of over 50 $\mu$s.

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and then propagating and accelerating along the channel. The initial flamefront velocity exceeded $1500\text{ m s}^{-1}$ and accelerated to $2000\text{ m s}^{-1}$ at the channel outlet. The corresponding data points are plotted in the $x$–$t$ diagram in the negative $x$-values region. It is seen that the $x$–$t$ trajectory of the flame inside the discharge channel agrees well with the one inside the detonation tube. The dashed line in the diagram is plotted to better illustrate the acceleration of the flamefront inside the channel.

An experimental study of detonation initiation by high-voltage, nanosecond gas discharge has been performed in a smooth detonation tube with a four-channel discharge chamber designed to enable a gradient initiation mechanism [59,60]. Stoichiometric propane–oxygen mixtures diluted by nitrogen were used at initial pressures from 0.2 to 1 bar. Detonation was formed within four transverse tube sizes at initial pressures higher than 0.2 bar for the propane–oxygen mixture and higher than 0.8 bar for the diluted mixture with 40 per cent nitrogen (figure 17). The discharge energy inputs were 0.2–0.3 J. The time of detonation formation was below 0.5 ms for all conditions. The value of the ignition delay time gradient, formed by non-uniform radical production during streamer discharge and following rapid plasma thermalization, has been estimated.

(i) Role of the gradient mechanism

According to the gradient initiation mechanism theory, the condition for the gradient mechanism to lead to detonation-wave formation is that the spontaneous combustion velocity $D_{sp}$ is greater than the sound speed $V_s$ and less than the CJ velocity $D_{CJ}$. The spontaneous combustion velocity $D_{sp}$, or the ignition pattern inside the discharge channels in general, is determined by the temperature gradient and by the distribution of radicals produced by the discharge. Knowing the temperature and estimating the radical concentration at different points along the channel, it is possible to evaluate the corresponding ignition delay
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Figure 18. Calculated O atom concentration distribution over the interelectrode gap, corresponding to Zeldovich’s model (dashed line) and the modified Zeldovich criterion (solid line). Propane–oxygen with 40% nitrogen. HV, high-voltage; FWHM, full-width at half-maximum. (Online version in colour.)

Taking into account that \( D_{\text{sp}} = (\frac{\text{d}T}{\text{d}z})^{-1} \), where \( z \) is the axial coordinate along the channel, we can estimate whether Zeldovich’s gradient condition can be fulfilled. To estimate the absolute values of these parameters, energy branching of the 200 mJ put into the gas by the discharge was considered. According to the model of energy exchange in non-equilibrium plasma, described above, 20–30% of the energy input is branched into direct heating of the gas by rapid thermalization mechanisms. As for the radical production, it has been shown [32] that O atoms are produced at an overall energy cost of approximately 8 eV.

The peak temperature increase was \( \Delta T \sim 700 \text{K} \), and the peak atomic oxygen production was 3.5%. The chemical kinetics calculation performed under these conditions using the reaction mechanism described by Zhukov & Starikovskii [21] yields an ignition delay time of 33 ms, which agrees with the experimentally observed result.

The results are shown with a dashed line in figure 18, together with the experimental distribution. The condition on the gradient holds if the slopes of the two curves coincide in some region, but in general, Zeldovich’s criterion requires a much weaker gradient than the experimentally observed one.

It should be noted, however, that Zeldovich’s criterion was introduced using the conditions of ‘weak’ excitation with rather slow energy release in chemical reactions. Under the conditions of high-voltage, high-current pulsed discharge, the excitation is rather strong, and the chemical energy release time becomes comparable or even less than the gas-dynamic time. Under these conditions, we should take into account the ignition delay time profile variation owing to propagation of strong compression waves from the reaction.
zone. It changes the Zeldovich conditions significantly, assuming a constant ignition delay time gradient during the entire DDT process. The basic difference between the proposed criterion modification and Zeldovich’s original model is a consideration of the compression wave influence on the ignition delay time distribution. It is assumed that ignition occurs near the tip of the high-voltage electrode. Fast energy release (faster than the gas-dynamic expansion time) will lead to temperature, pressure and sound-speed increases in this gas volume. The parameters of this high-pressure, high-temperature gas are: pressure, $P_4$; temperature, $T_4$; sound speed, $a_4$; and specific heat ratio, $\gamma_4$. The initial parameters of the gas in the vicinity of the ignition point are: pressure, $P_1$; temperature, $T_1$; sound speed, $a_1$; and specific heat ratio, $\gamma_1$. Thus, we have a common task of arbitrary discontinuity, which has a well-known solution,

$$\alpha = \frac{p_4}{p_1} = \frac{2\gamma_1 M_s^2 - (\gamma_1 - 1)}{\gamma + 1} \left[ 1 - \frac{\gamma_4 - 1}{\gamma_1 + 1} a_4 \left( M_s - \frac{1}{M_s} \right) \right]^{-2\gamma_4/(\gamma_4 - 1)}$$

with the formation of a shock wave with a propagation velocity $M_s$. From this equation, one can derive $M_s = \vartheta(\gamma, \alpha)$. The shock wave generated by the energy release at the initiation point will propagate through the gas, increasing its temperature, pressure and density [62],

$$\frac{T_2}{T_1} = 1 + \frac{2(\gamma - 1) \gamma M_s^2 + 1}{(\gamma + 1)^2 M_s^2 - 1} = \Psi(\gamma, \alpha).$$

We need to increase the temperature in a new point at a distance $L$ from the point of initiation to the initial value in the point of initiation,

$$T(L) = \frac{T(0)}{\Psi(\gamma, \alpha)}.$$

However, the temperature gradient is

$$\frac{\Delta T}{\Delta x} = \frac{T(0) - T(L)}{L} = T(0) \frac{1 - 1/\Psi(\gamma, \alpha)}{L}.$$

By using an obvious estimation for $L$ of $L = \tau_E M_s c = \tau_E \vartheta(\gamma, \alpha) c$, where $\tau_E$ is the chemical energy release time, $M_s$ the shock-wave Mach number and $c$ the sound speed in the gas, one can derive a modified Zeldovich’s criterion for the case of strong initial perturbations in the reactive system and short energy release time, leading to chemical energy release at almost constant-volume conditions,

$$\frac{\Delta T}{\Delta x} = T(0) \frac{1 - 1/\Psi(\gamma, \alpha)}{\tau_E \vartheta(\gamma, \alpha) c} \approx 10 \text{ K mm}^{-1}, \quad (3.1)$$

where for $\tau_E$, we used the experimentally observed value $\tau_E \sim 40$ ms (theoretical estimations give the same value). $T(0)$ was defined as the initial gas temperature after the discharge $T(0)$, approximately 900 K. All other values were found from the equations above.

For typical mixtures used in the current work, it is easy to estimate all parameters in equation (3.1). The estimations give $dT/dx \sim 10 \text{ K mm}^{-1}$. This gradient is also shown in figure 18 as the modified model, together with the original Zeldovich criterion. As expected, the modified criterion requires a much

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shorter gradient because of the compression wave influence on the mixture to the right of the initiation point. Of course, the good agreement between the modified Zeldovich criterion and the experimentally measured gradient is rather coincidental because of the unsteady nature of the interaction. However, this correlation shows that this interaction can really modify the optimal ignition delay time distribution and can bring it very close to the experimentally observed distributions (figure 18).

4. Summary

Non-equilibrium plasma demonstrates great potential to control ultra-lean, ultra-fast, low-temperature flames and to become an extremely promising technology for a wide range of applications, including aviation GTEs, piston engines, RAMjets, SCRAMjets and detonation initiation for PDEs. To use non-equilibrium plasma for ignition and combustion, it is necessary to understand the mechanisms of plasma-assisted ignition and combustion under various conditions and to numerically simulate discharge and combustion processes under various conditions.

Two general mechanisms of DDT initiation by a non-equilibrium plasma of distributed discharges were analysed. In the case of radial propagation of the discharge with a low discharge power density, a slow flame was formed, and for successful DDT, additional mechanisms (gas-dynamic perturbations) were required. For longitudinal discharges with a high power density in a plasma channel, two fast DDT mechanisms have been observed.

When initiated by a spark or a transient discharge, the mixture ignited simultaneously over the volume of the discharge channel, producing a shock wave with a Mach number greater than 2 and a flame. The delay between the shock-wave and flame formation was governed by the energy transferred to translational degrees of freedom and by radical formation. The waves then formed an accelerating complex, resulting in DDT. At an initial pressure of 1 bar, the DDT length and time did not exceed 50 mm and 50 μs, respectively, for propane–oxygen–nitrogen mixtures.

A gradient mechanism of DDT similar to that proposed by Zeldovich has been observed experimentally under streamer initiation. The mixture inside the discharge channel was excited non-uniformly by the streamer, thus forming an excited species concentration gradient. The gradient corresponded to that of the ignition delay time. The hottest spot with the shortest ignition delay was at the high-voltage electrode tip. Originating at this point, the spontaneous combustion wave started propagating along the channel at a velocity over 1500 m s⁻¹ and accelerated up to the CJ velocity value at the channel output. The initiation energy was lower for the streamer mode by an order of magnitude compared to the spark initiation under experimental conditions, whereas the DDT time was three times longer. However, the DDT length was still within 50 mm, which corresponded to two transverse tube sizes, and the DDT energy was lower than the energy of direct planar detonation initiation by two orders of magnitude. The extremely short DDT distances under reasonable energy input values achieved owing to the gradient mechanism are a prerequisite for the design of compact and efficient PDEs.
Thus, plasma-assisted ignition might be an effective tool in different applications, including high-speed, ultra-lean combustion and control of transient combustion processes, such as DDT.

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