Repetitive streamer discharges leading to Ignition of hydrogen/air mixtures

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Abstract

Repetitive streamer discharges due to high-frequency AC voltage can ignite H_2/air mixtures and are the focus of research concerning the explosion protection of electrical apparatuses. The ignition process is not understood in detail. In streamer discharges, a non-equilibrium plasma occurs leading to the formation of chemically active radicals, such as atomic oxygen and atomic hydrogen as well as hydroxyl. The influence of the radical build up during repetitive streamer discharges on the ignition process is examined. Using detailed chemical kinetics describing the discharge phase and its afterglow, the ignition of H_2/air mixtures is studied. The influence of the reduced electric field and the electron density on the ignition is examined numerically.

1. Introduction

As an assessment basis for electrical apparatuses to be used in harzardous areas, the supply voltage is used, whereby transient overvoltages are not taken into account[1]. In electrical supply networks, however, transients which are due to switching operations with high-frequency overvoltages may occur and put stress on the insulation system of electrical equipment. In the case of converter-fed drives, on long lines, transients with high-frequency overvoltages occur, too. These overvoltages can cause streamer discharges, which have proved to ignite H_2/air mixtures and are, therefore, the focus of research concerning the explosion protection of electrical apparatuses[2),3]. However, the ignition process is not understood in detail.

In streamer discharges, a non-equilibrium plasma occurs with the electrons having significantly higher plasma temperatures than the other gas components[4]. Hence, the high energy electrons lead to the excitation of different electronic states. Eventually, some of these electronic states result in the dissociation of gas components and, thus, the forming of chemically active radicals like atomic oxygen, atomic hydrogen and hydroxyl, as shown by Starikovskaia[4] and Bowman et al.[5]. The rate coefficients of these reactions strongly depend on the reduced electric field. In addition to the formation of radicals, a temperature increase in the streamer channel due to the repetitive character of the discharges can be expected. According to Starikovskaia[4] it is in the range of tens of kelvin for each streamer discharge. Both the formation of radicals and the temperature increase in the streamer channel lead to the ignition of the H_2/air mixture[6].

Bozhenkov et al.[7] shows in experiments and simulations a significant ignition delay time reduction (by more than an order of magnitude) using a single pulse high voltage nanosecond discharge in H_2/air mixtures diluted in argon. The non-equilibrium course of the discharge was regarded. The reduced electric field for the simulations was 300 Td.

In the review article of Starikovskaia[4] concerning plasma assisted ignition and combustion, the impact of different kinds of discharge plasmas on the ignition process and combustion, respectively, is discussed. It was pointed out that even small amounts of radicals (~10^{-5-}

10^{-3} of the total number of the gas particles) can significantly influence the ignition.

Popov[6] presents a reaction mechanism regarding ionization, dissociation and excitation of gas molecules in a H_2/air mixture in consideration of a pulsed high-current discharge having a maximum reduced electric field of 1400 Td in low pressure (5torr) stoichiometric H_2/air mixtures. It was concluded that the explosion limit of a combustible mixture can be significantly reduced by introducing radicals using non-equilibrium discharges, although this effect only arises near the ignition threshold. Also, the temperature at which ignition occurred decreased by almost 300 K, leading also to a decrease in the ignition delay time (both compared with autoignition).

Bowman et al.[5] considered the kinetics of low-temperature hydrogen oxidation and ignition by repetitively pulsed non-equilibrium plasmas (frequency 10 kHz - 40kHz) in H_2/air mixtures having a maximum reduced electric field of 250 Td at pressures up to 40 torr. The kinetic model used was validated by comparing the measured time-resolved OH mole fraction using LIF and time-resolved absolute atomic number density of O using TALIF with numerical results. Thereby, it was shown experimentally und numerically that the O atom density increases with the number of pulses.

In our previous work[3] we examined the ignition of different H_2/air mixtures at atmospheric pressure due to streamer discharges caused by high-frequency voltage (frequency 600 kHz - 800kHz, maximum voltage amplitude up to 20 kV). The number of voltage cycles at 11 kV and 740 kHz necessary to ignite H_2/air mixtures (volume fraction of 10 % - 70 % H_2 in air) was studied. The streamer action was considered as gas heating only, thereby neglecting the non-equilibrium course of the discharge in a first step.

In this paper, the ignition of H_2/air mixtures is investigated numerically using detailed chemical kinetics and taking the non-equilibrium course of the streamer discharge plasma into account. Using the Bolsig+ software and database[8], the electron distribution in the H_2/air mixtures is determined, taking into account the acceleration of the electrons in the electric field, on the one hand, and the momentum loss and energy loss of the electrons in collisions with neutral gas particles, on the other hand. The collision cross sections are given in the Bolsig+ database.

By solving the electron Boltzmann equation in the classical two-term approximation, the rate coefficients of the dissociation of oxygen and hydrogen are determined as well as different excited states of oxygen, hydrogen and nitrogen for different reduced electric fields[9]. Hence, the production of radicals and many excited states in the burst of streamer discharges can be calculated. The non-equilibrium H_2/air plasma mechanism used is given by Bowman et al.[5]. It is based on a non-equilibrium air plasma model specified by Kossyi[10], expanded to include the hydrogen dissociation processes and hydrogen/oxygen chemistry[6].

The paper is structured as follows:

In section 2, a short description of the experiment is given. In section 3, the numerical model used for the calculations is explained before the results are presented in section 4. Finally, in section 5, our conclusions are drawn.

2. Experiment

A schematic view of the test set-up is presented in Fig. 1 a). The experimental set-up is described in detail in Langer et al.[3]. In addition to this description, LIF measurements of OH can be performed as explained in Markus et al.[11]. An alternating voltage is given to a rod/plane configuration in which the plane is grounded. If positive voltage is supplied to the rod intensive streamer discharges occur for approximately 100 ns as can be seen in Fig. 1b). In the case of a negative rod, a discharge can be observed, too, but less intensively and with not as much propagation[3].

The streamer discharges lead to the ignition of H_2/air mixtures in dependence on the number of voltage cycles for a given maximum voltage amplitude. In Fig. 1c), the
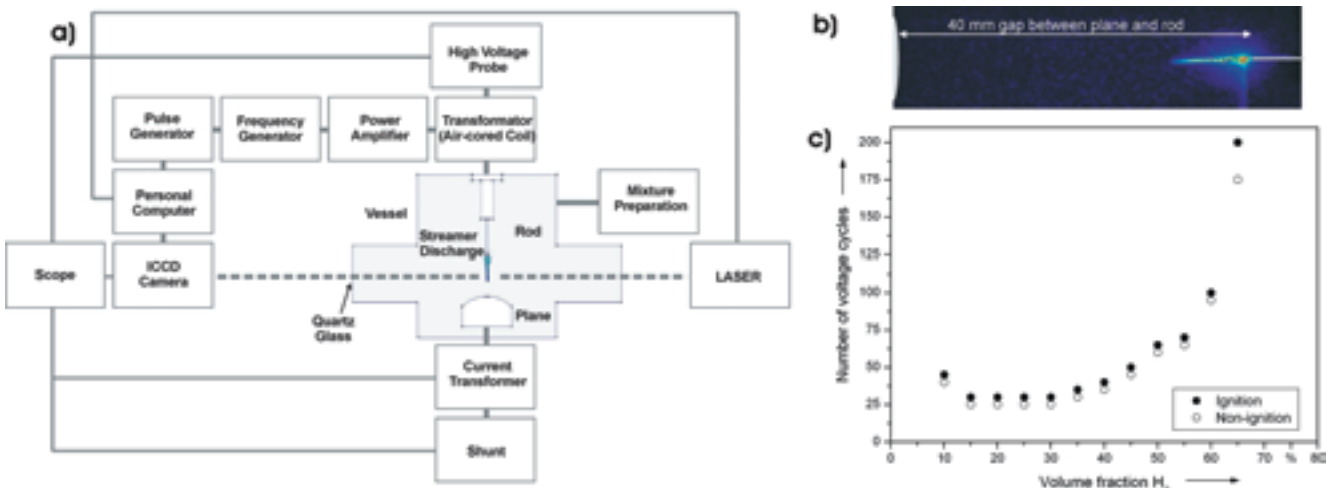

Fig. 1   a) Schematic view of the test-up; b) Streamer discharge in air photographed using an ICCD camera after 100 voltage cycles at a maximum voltage amplitude of 9kV (exposure time 40 ns); c) Minimum voltage cycles necessary to ignite different H_2/air mixtures at a voltage amplitude of 11 kV (Langer et al. (2010)).

dependence can be seen for a voltage amplitude of 11 kV (740 kHz) and different H_2/air mixtures. More voltage cycles are necessary to ignite the mixture composition if it is leaner or richer compared with the most ignitable composition of 22 % H_2 in air[12]).

3. Numerical Model

The influence of repetitive streamer discharges on H_2/air mixtures at atmospheric pressure is considered. The oscillation period is assumed to be 1300 ns (frequency 769 kHz), which is in good accordance with the period of 1350 ns (740 kHz) used in the experiments presented in Langer et al.[3]. As the measurements show, only during approximately 100 ns is it possible to observe an intensive streamer formation. How many streamer discharges are formed exactly during this time remains unclear. Therefore, the shape of the reduced electric field is assumed to be a square pulse during the 100 ns and not to exist in the other 1200 ns (see Fig. 2). The discharges occurring when the rod is supplied with negative voltage are neglected as well as the temporal variation of the external electric field. The electric field distribution was calculated for the rod/plane configuration in Langer et al.[3]. The calculated reduced electric field following from that consideration showed that a reduced electric field between 100 Td to more than 300 Td can be expected close to the rod. According to Starikovskaia[4], the reduced electric field in the streamer head is between 90 Td and 300 Td.

The model of a perfectly stirred reactor is used to calculate the time dependence of the different species and the ignition delay time of the H_2/air mixture under homogeneous conditions[13]. The ignition process is considered in dependence on the temperature and, in our case, on the mixture composition with all excited species. Heat conduction and diffusion is not taken into account. Thus, it is neither necessary to assume an ignition energy nor a streamer volume which, therefore, represents a minimal influence of the experimentally achieved results on the numerical results. It enables focusing on the formation of different species and their influence on the
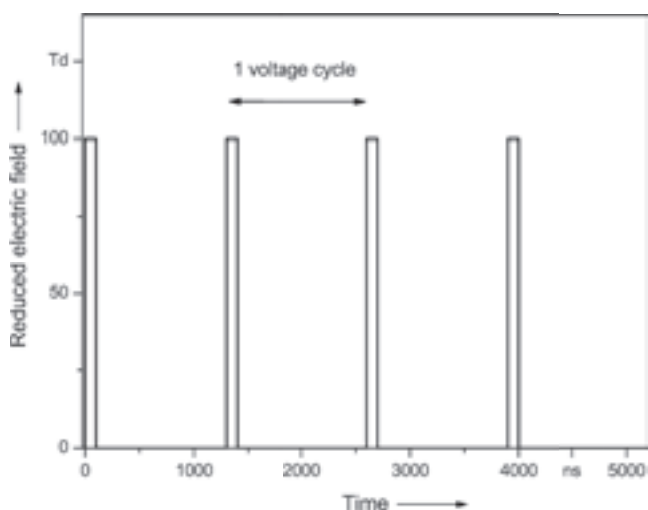

Fig. 2   Assumed square pulses of the reduced electric field for the numerical calculation.

ignition process in dependence of important parameters such as the electron density and the reduced electric field strength. Naturally, the energy deposition along the streamer channel cannot be assumed to be homogeneous. In fact, the energy deposition is the most near the tip of the rod since ignition is observed in this part of the streamer channel[3),11]. Furthermore, Ono and Oda[14] showed that the highest temperatures can be expected near the tip of the rod.

In order to regard the formation of excited atomic and molecular states, a detailed mechanism is needed to describe the non-equilibrium plasma action during the time when a reduced electric field is assumed to be present and excitation processes take place. Afterwards, during the 1200 ns in the afterglow of the discharge, quenching of excited atoms and molecules takes place and needs to be considered. Additionally, the reactions describing the hydrogen oxidation are included. The reaction mechanism used in this paper is the one given by Bowman et al.[5]. It incorporates 124 equations to calculate the temporal formation of $O(^3P)$, $O(^1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, $O_2(c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+)$, O_2, $H(^1S)$, H_2, $N(^4S)$, $N(^2P)$, $N(^2D)$, $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(C^3\Pi_u)$, $N_2(a'^1\Sigma_u^-)$, N_2, O_3, NO, NO_2, NO_3, N_2O_4, N_2O_5, N_2O, OH, H_2O, HO_2, H_2O_2.

The rate coefficients of the reactions where electrons are involved are calculated using the Bolsig+ software[8]. A temperature dependence on the rate coefficients in these reactions can be neglected, since the energy electrons may gain in elastic collisions with gas particles is small compared with the electron energy gain in the electric field. So, the gas temperature noticeably influences the rate coefficients only in very low reduced electric fields. Therefore, all rate coefficients used are calculated at 300 K.

The ionization of molecules is not regarded in the mechanism. The electron density remains constant and is considered according to Starikovskaia[4].There, an electron density between 10^{11}-10^{12} cm^{-3} is indicated for streamer discharges. Other authors[15),16)] state values between 10^{14} cm^{-3} and 10^{15} cm^{-3} and 10^{16} cm^{-3}, respectively, in the case of accompanying thermalisation in the streamer volume[17].

According to Popov[6], the experimentally observed ignition cannot be an effect of the non-equilibrium course of the discharge plasma only. Therefore, for this study the temperature of the mixture is increased by 20 K after each voltage cycle. This is in accordance with the work of Starikovskaia[4] that the gas heating in the volume which is affected by a streamer discharge is not larger than tens of kelvin.

4. Results

Using OH-LIF, the ignition delay time after 30 voltage cycles at 11 kV could be estimated to be less than 120 μs for a 25 % H_2 in air mixture[11]. For further considerations, the ignition delay time of approximately 120 μs is the parameter to compare the results of experiment and simulation. The temporal mixture composition is calculated regarding the full set of reactions - thus, especially the non-equilibrium plasma action (dissociation,
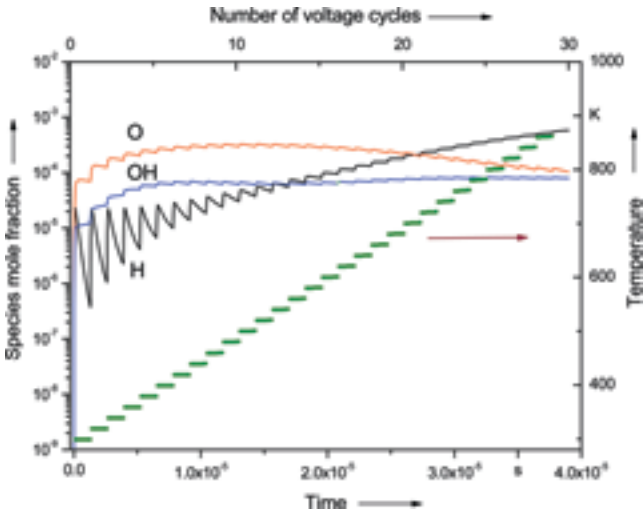
Fig. 3 Atomic oxygen, atomic hydrogen and hydroxyl formation during 30 voltage cycles in a 25% H_2/air mixture, together with the temperature increase in the streamer volume.

excitation) with the gas molecules is included for 100 ns. During the rest of the voltage cycle (1200 ns) no reactions containing electron impact are regarded in the calculation. The electron density is $10^{12} cm^{-3}$. The reduced electric field during the assumed 100 ns square pulse is 100 Td.

In Fig. 3 the radical formation of O, H and OH is presented for a burst of 30 voltage cycles. Moreover, the assumed temperature increase during the voltage cycles is presented. At the beginning, the temperature of the mixture is 300 K. After each cycle (1300 ns) the temperature is increased by 20 K (set to the higher value). Therefore, the final temperature after 30 cycles is 880 K.

After the first discharge phase it can be seen in Fig. 3 that more O is formed than H. During the first afterglow the H is rapidly degraded. The mole fraction drops more than one order of magnitude, whereas the mole fraction of O remains almost constant. The mole fraction of OH increases during the discharge and the afterglow phase. For the next few voltage cycles the mole fraction of H after the discharge increases only slightly, while O and OH are approaching their limit value. The highest O mole fraction is reached during the 13th voltage cycle at a temperature of 520 K. The OH mole fraction remains almost constant after six voltage cycles. In contrast, the H mole fraction increases during all 30 cycles. Altogether, it can be seen that the amount of O, H and OH is in the order between 10^{-5}-10^{-3} of the total number of gas particles, as was stated by Starikovskaia[4].

For different temperatures, a sensitivity analysis concerning the formation of O, H and OH was performed. The main facts are presented. The formation of O, H and OH in the discharge phase is most sensitive to the reactions with electron impact for temperatures up to 600 K, thus, mainly to
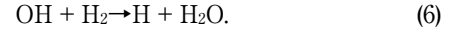
$$O_2 + e- \rightarrow O + O + e- \qquad (1)$$

$$O_2 + e- \rightarrow O + O(^1D) + e- \qquad (2)$$

$$H_2 + e- \rightarrow H + H + e-. \qquad (3)$$
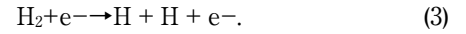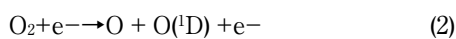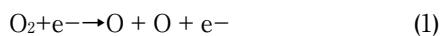
In the afterglow phase at 300 K - 500 K the formation of O is most sensitive to the quenching of $N_2(A^3\Sigma_u^+)$, resulting in dissociation of O_2 :

$$N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2 + O + O. \qquad (4)$$
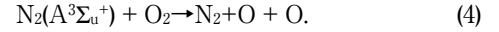
Between 500 K - 700 K it is most sensitive to reaction (5) in which NO is formed :

$$N + O_2 \rightarrow NO + O. \qquad (5)$$
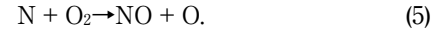
The most sensitive reaction up to 800 K concerning the formation of H is the reaction

$$OH + H_2 \rightarrow H + H_2O. \qquad (6)$$

Starting at 500 - 600 K, also the thermally controlled chain branching reactions become important concerning the formation of O, H and OH. Therefore, the influence of reactions (7) and (8) increase with increasing temperature :

$$H + O_2 \rightarrow O + OH \qquad (7)$$

$$O + H_2 \rightarrow H + OH. \qquad (8)$$

After 30 voltage cycles no more voltage is supplied to the rod. Hence, only the set of reactions without electron impact is used to calculate the onward process of the mixture. The ignition delay time, which includes the voltage supply time, is studied and compared with the experimentally achieved result of approximately 120 µs using OH LIF. In Fig. 4, the temporal temperature course showing the ignition can be seen. The ignition delay time is 120 µs.

To observe ignition delay times in the order of 100 µs, a temperature of approximately 1100 K is needed with regard to autoignition for a 25% H_2/air mixture[18]. Therefore, regarding the non-equilibrium course of the discharge - which is not considered in the case of autoignition - the temperature in the streamer volume necessary to ignite the mixture (having the same ignition
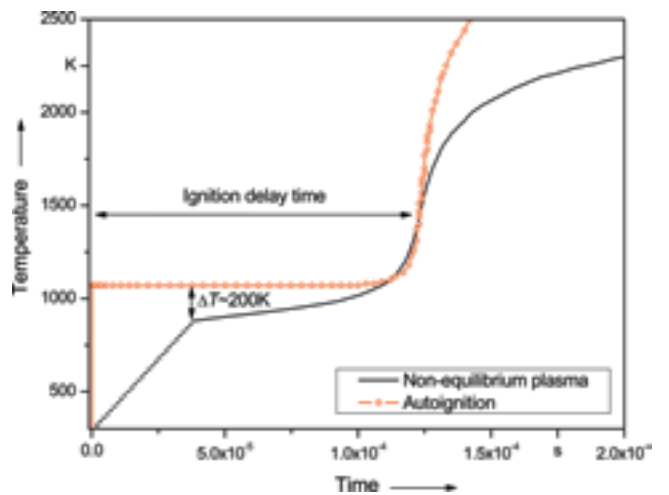

Fig. 4 Temperature course of an ignition of a 25% H_2/air mixture after 30 voltage cycles under the same conditions as used in Fig. 3 for the non-equilibrium impact and considering autoignition (ignition delay time in both cases 120 µs).

delay time) decreases significantly about 200 K in the example shown in Fig. 4, compared to autoignition.

The results presented in Fig. 3 and Fig. 4 strongly depend on the electron density, the reduced electric field, the temperature increase after each cycle and the time in which the formation of streamer discharges is assumed during one voltage cycle. For these parameters, reasonable intervals can be defined following from the literature or own measurements. But to understand how these parameters influence, the result it is studied how a variation of these parameters affects the result in principle.

In Fig. 5 the dependence of the electron density on the number of voltage cycles necessary to ignite a mixture with the same initial values as used in the calculations for Fig. 3 and the non-equilibrium case in Fig. 4 (except the electron density) is presented. To compare the results with the results of Fig. 3 the criterion chosen is that the ignition delay time has to be within an interval of $120\mu s \pm 12\mu s$. All other parameters are kept unchanged. As can be seen in Fig. 5, the necessary number of voltage cycles to ignite the mixture decreases with increasing electron density. Additionally it needs to be taken into account that the temperature increases 20 K after each cycle. So not only are fewer voltage cycles necessary to ignite the mixture but also the temperature at which ignition occurs decreases with increasing electron density. The result at $10^{12} cm^{-3}$ (880 K) represents the result of Fig. 3 and Fig. 4. Increasing the electron density, which is consistent with the electron densities given in the literature[15)−17)] leads to ignition at fewer voltage cycles and lower temperatures. For example, in the case of $5 \cdot 10^{13} cm^{-3}$ ignition (ignition delay time $108\mu s$) occurred after 25 voltage cycles at a temperature of 780 K. Hence, the temperature is about 300 K lower compared to the autoignition temperature, which leads to ignition with an ignition delay time in the order of $100\mu s$. Decreasing the electron density to $5 \cdot 10^{11} cm^{-3}$ leads to ignition after 33 voltage cycles (ignition delay time 109 μs) at a temperature of 940 K. The reason is that by increasing the electron density, the formation of radicals and excited states in molecules, which enhance the ignition process, is increased also.

In Fig. 6, the dependence of the reduced electric field strength on the number of voltage cycles necessary to ignite the same mixture as used in Fig. 3 and Fig. 4 (except the rate coefficients for the reactions where electrons are involved) is presented. The ignition delay time of $120\mu s \pm 12\mu s$ is again the criterion to compare the results. As can be seen in Fig. 6, the necessary number of voltage cycles to ignite the mixture decreases with increasing reduced electric field. The result at 100 Td represents the result of Fig. 3 and Fig. 4. For 300 Td, which is within the interval indicated by Starikovskaia[4)], ignition occurred after 26 voltage cycles (ignition delay time $120\mu s$) at a temperature of 800 K. At a reduced electric field of 50 Td, 35 voltage cycles are necessary (ignition delay time $120\mu s$, temperature 980 K) to ignite the mixture. The reason is that by increasing the reduced electric field the rate coefficients of the reactions with electron impact are
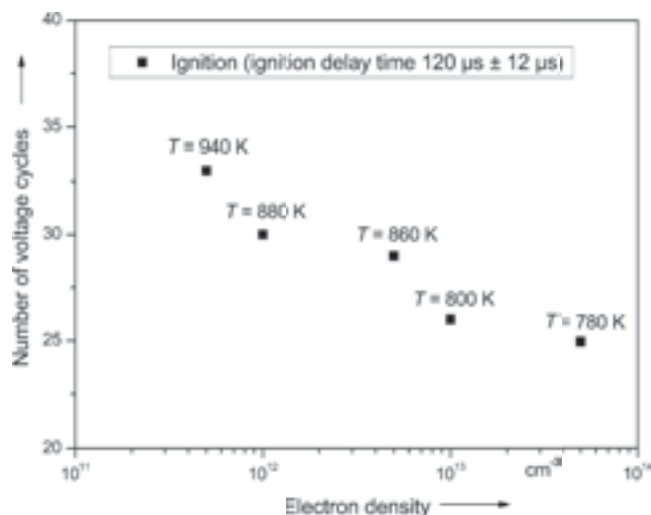

Fig. 5 Dependence of the assumed electron density in the streamer volume on the necessary number of voltage cycles to ignite a 25% H_2/air mixture at a reduced electric field of 100 Td.
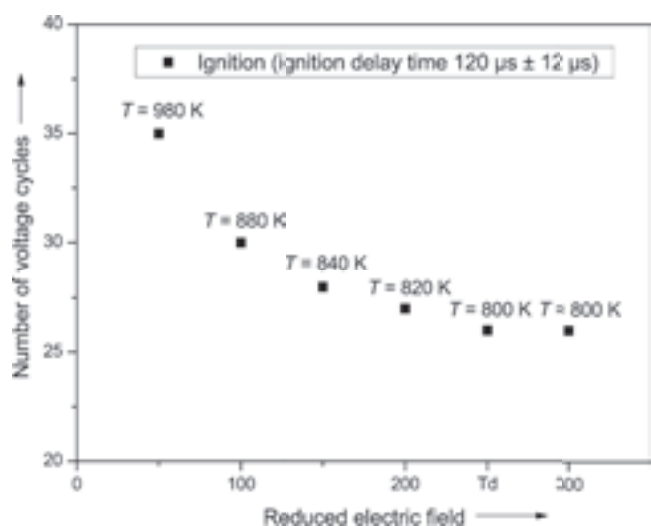

Fig. 6 Dependence of the reduced electric field strength in the streamer volume on the necessary number of voltage cycles to ignite a 25% H_2/air mixture at an electron density of 10^{12} cm^{-3}.

increased. Hence, more radicals and excited molecular states are formed, which then enhance the ignition process.

5. Summary and Conclusion

Using detailed chemical kinetics describing the streamer discharge and its afterglow, the ignition of H_2/air mixtures is studied. Thereby, the spatial energy deposition in the streamer channel is neglected. However, the approach enables to study the influence of important parameters such as the electron density and the reduced electric field. During the repetitive streamer discharges an amount of $10^{-5}−10^{-3}$ of the radicals O, H and OH, compared to the total number of particles, is formed. The reactions being most sensitive to the formation of O, H and OH formation and consumption were analyzed. A sensitivity analysis concerning the formation of O, H and OH showed that during the discharge phase reactions with electron impact are most sensitive, whereas during

the afterglow phase reactions regarding the quenching of excited states and the formation of NO are important before thermally controlled chain branching reactions at higher temperatures become most sensitive.

The influence of electron density and the strength of the reduced electric field was examined. Increasing the electron density or the reduced electric field strength leads to a decreasing number of voltage cycles necessary to ignite the H_2/air mixture. Both parameters strongly influence the amount of radicals and excited molecules formed. Regarding the non-equilibrium course of the discharge ignition occurs at lower temperatures compared with autoignition. The observed ignition temperature decrease can be as much as 300 K. In summary, it can be stated that a non-equilibrium plasma in the streamer discharges significantly influences the ignition process.

The temperature increase after each voltage cycle and the time in which the formation of streamer discharges is assumed during one voltage cycle will be studied in the future as well as the ignition of other mixture compositions of H_2/air. The results will improve the knowledge about the ignition process due to streamer discharges and, therefore, provide valuable knowledge for the explosion protection of electrical apparatuses.

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